Optical spectra of CuO_2 and matrix effect upon its structure

Nico Caspary

Infineon Technologies, D-81739 München, Germany

Elena V. Savchenko[*]

B. Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine
47 Lenin Ave., Kharkov 61164, Ukraine

Anton Thoma and Andreas Lammers

Teradyne GmbH, D-81673 München, Germany

Vladimir E. Bondybey

Institut für Physikalische und Theoretische Chemie der TU München, 85747 Garching, Germany
E-mail: bondybey@ch.tum.de

Optical absorption and laser induced fluorescence (LIF) spectra of CuO_2 in solid matrices have been investigated, and previous visible studies were extended into the infrared. Several new electronic states were observed and their vibrational frequencies determined. The matrix data are compared with the results of recent gas phase CuO_2^- photodetachment studies, and with ab initio calculations. We also discuss the unusually large matrix effects and medium-induced electronic and vibrational frequency shifts observed for CuO_2.

PACS: **33.20.**−t, 33.50.Dq

1. Introduction

Copper oxides, and CuO_2 in particular, are interesting species, which have been studied quite extensively. One of the first laser induced fluorescence studies in rare-gas matrices in fact involved the CuO_2 molecule [1]. A strong visible absorption, and an intense fluorescent progression observed when matrices containing copper were irradiated by the 488 nm line of an argon ion laser were originally actually attributed to the diatomic CuO. The same spectrum was later reexamined by several other investigators, and the observed unusually large vibrational frequency shift compared with the known CuO gas phase value remained a mystery for more than a decade [2,3]. In 1982 Tevault showed with the help of isotopic substitution conclusively that the emitter actually contains two oxygen atoms [4]. A subsequent reexamination of the fluorescence using a tunable pulsed dye laser then revealed that the molecule is in all probability linear and centrosymmetric, with the observed progression involving the totally symmetric Cu−O stretching vibration [5]. In the same neon matrix study the bending frequencies both in the ground state and in the excited electronic state could be also identified.

Numerous theoretical studies of copper oxides have suggested that at least two isomeric forms of the CuO_2 dioxide should exist, the covalent linear centrosymmetric species, and a Cu−O_2 complex. While the theoretical studies suggested a C_{2v}, T-shaped geometry for the latter isomer [6,7], probably the global minimum on the CuO_2 potential surface, the experimental evidence seems to favor two nonequivalent oxygen atoms and a C_s symmetry for the complex. Theoretical investigations of the inserted, covalent form yielded a linear compound with a $D_{\infty h}$ symmetry [8,9], and the recent

CASSCF study of Mochizuki et al. also predicted the existence of numerous low-lying excited electronic doublet states [10,11].

The existence of two CuO_2 isomers was confirmed experimentally in the gas phase by a recent photodetachment study of Wu et al. [12,13]. These authors detected the bent complex species with a detachment energy of about 1.5 eV, while the linear CuO_2 has a much higher electron affinity around 3.45 eV. In agreement with the theoretical prediction, they also detected several low-lying excited electronic states, with at least three of them located within less than 1 eV above the ground state. Most recently, Chertihin et al. have reexamined copper oxides in solid argon, and observed a closely spaceddoublet infrared absorption at 823.0 and 818.8 cm^{-1} [9].This they assigned to the asymmetric stretching vibration of the symmetric CuO_2 isomer based on its behavior, and on the appearance of a triplet of such doublets with relative intensity ratios of 1:2:1 in experiments employing an oxygen sample enriched to 50% with ^{18}O.

Over many years we frequently observed spectra of the symmetric CuO_2 species while using a laser vaporization technique developed in our laboratory. The oxide was also always produced whenever copper electrodes were used in our pulsed discharge technique. The copper atom apparently does not spontaneously insert into a ground state oxygen molecule, but the oxide forms efficiently by reaction of translationally or electronically excited copper atoms produced by the laser vaporization or the cathode sputtering processes. During these studies, we made a variety of new observations, and several new and puzzling effects emerged. These results are reviewed, interpreted and summarized in this manuscript.

2. Experimental

2.1. Fluorescence of CuO_2 and its ground-state structure

We examined the spectra in a number of different matrices, neon, argon, krypton and xenon, as well as in solid N_2. The spectra exhibit interesting medium effects, which will be discussed later, and their interpretation is complicated by the presence of multiple sites. In solid xenon the spectra are least obscured by such multiple «site effects», and we will therefore focus our initial discussion on this matrix.

Typical CuO_2 absorption spectra in solid xenon obtained using $^{16}O_2$ and $^{18}O_2$, respectively, are shown in Fig. 1,a and b. Each spectrum reveals a strong progression involving the upper-state sym-

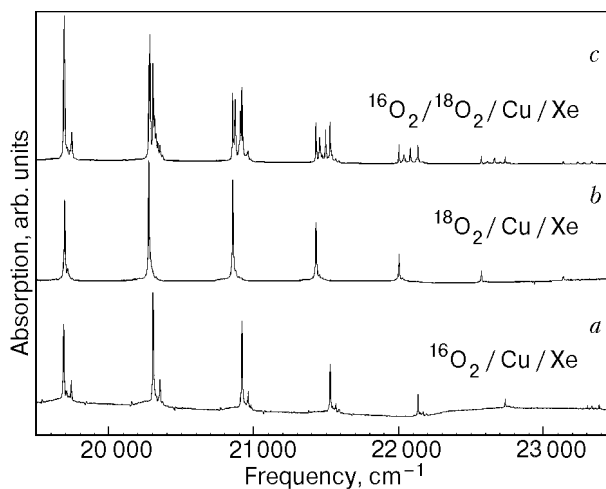Fig. 1. Absorption spectra of different CuO_2 isotopomers in a xenon matrix. The upper trace contains $^{16}OCu^{16}O$, $^{16}OCu^{18}O$ and $^{18}OCu^{18}O$ in a ratio of approximately 1:1.5:1. The matrices of the two lower spectra were generated from the pure isotopic gases and contain therefore only $^{16}OCu^{16}O$ (a) and $^{18}OCu^{18}O$ (b), respectively. The side bands in a can be seen as site effects.

metric stretching frequency ν_1, but even in xenon one can detect numerous much weaker bands mainly due to minor sites. Excitation of the individual vibronic bands produces the well-known intense fluorescence spectrum of the CuO_2 oxide. This is shown for the two isotopic molecules in Fig. 2,a and c. While the observed bands can easily be fitted to obtain spectroscopic constants for either of the two isotopic species individually, if one attempts a global analysis including the data for both isotopes, a very poor fit with large systematic errors results. All the bands of $Cu^{16}O_2$ are computed some
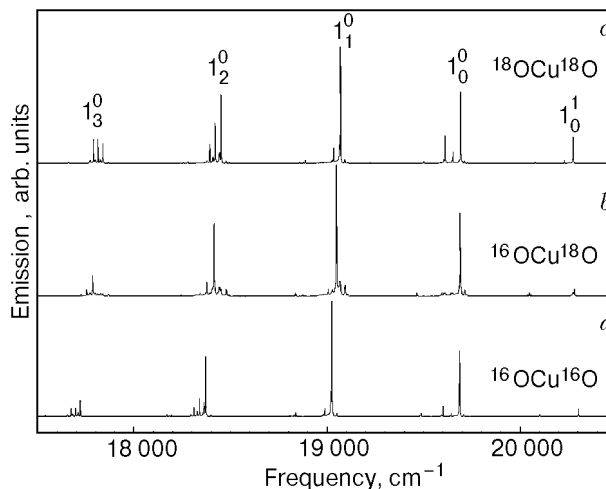

Fig. 2. Comparison of the laser-induced fluorescence spectra for three different isotopomers of copper oxide in a xenon matrix: $^{16}OCu^{16}O$ (a), $^{16}OCu^{18}O$ (b), and $^{18}OCu^{18}O$ (c). For each species the 1_0^2 state was excited. The assignments of the week transitions is shown in Fig. 3.
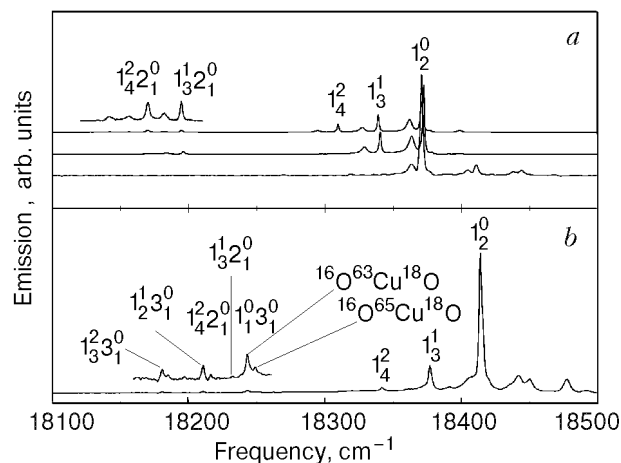
Fig. 3. Assignment of the week bands in the emission spectrum. Figure *a* shows some parts of the emission spectra of $^{16}OCu^{16}O$. The matrix was excited for the upper trace in the 1_0^2, for the middle trace in the 1_0^1, and for the lower trace in the 0_0^0 transition. Figure *b* shows the same spectrum for $^{16}OCu^{18}O$, excited in the 1_0^2 state.

2.5 cm^{-1} too high, and those of Cu^{18}O$_2$ too low by a comparable amount, clearly due to a zero-point energy problem and to the failure to include the other vibrational modes of CuO$_2$ in the fitting process.

The zero point energy difference contains information about the nontotally symmetric CuO$_2$ vibrations, and in particular about ν_3. The asymmetric stretching vibration ν_3 which is spectrally forbidden in an allowed electronic transition of the linear centrosymmetric CuO$_2$ should become weakly allowed and be in principle observable if the symmetry is lowered by asymmetric isotopic substitution. We have therefore carried out experiments with an equilibrated mixture of both oxygen isotopes, and obtained emission spectra for the third, asymmetric species $^{16}OCu^{18}O$, as shown in Fig. 2,*b*. As exemplified in the expanded section shown in Fig. 3, the spectrum indeed revealed additional emission bands which had no counterparts in the spectra of the pure, symmetric isotopic molecules. These bands, exemplified in Fig. 3 by the (0,0,0–0,0,1) transition, clearly involve the asymmetric stretching frequency ν_3. Unlike the main ν_1 progressions, the bands involving ν_3 exhibit distinct ^{63}Cu–^{65}Cu isotopic splitting, yielding values of 816.75 cm^{-1} and 812.6 cm^{-1} for the ν_3'' ground state vibration of the two copper isotopic species of $^{16}OCu^{18}O$ in solid xenon. From this a frequency of 830.8 cm^{-1} can be computed for ^{63}Cu^{16}O$_2$ which is consistent with the infrared absorption measurements of Chertihin et al. in argon matrices [9], and provides additional support for their assignment of the 823.0 cm^{-1} frequency they observed to the linear $D_{\infty h}$ CuO$_2$.

2.2. Vibrational structure of the excited E-state

A further problem emerges if one now tries to analyze and assign the absorption spectrum of the mixed isotopic molecule. An absorption spectrum observed in an experiment with a 1:1 mixture of $^{16}O_2$ and $^{18}O_2$ is shown in Fig. 1,*c*. Unlike the fluorescence spectrum, where one easily identifies groups of three approximately equidistant isotopic bands with an intensity ratio of 1:2:1, as one might expect for a molecule with two equivalent oxygen atoms, in absorption there seem to be groups of four bands of nearly equal intensities. Two of them are, based on the excitation spectra with pure isotopic samples, undoubtedly due to the symmetric species Cu^{16}O$_2$ and Cu^{18}O$_2$, respectively, but the remaining two absorption bands appear only when both isotopes are present, and are clearly due to the isotopically mixed molecules.

The question thus arises if there are two distinct $^{16}OCu^{18}O$ molecules, that is if the two oxygen atoms are not equivalent, or if the splitting is homogeneous, with two absorption bands appearing for each vibronic level of the mixed isotopic molecule. This question can be unambiguously answered by examining the emission spectra, and even more clearly with the help of a three-dimensional equal intensity plot of the type shown in Fig. 4. An examination of such plots is very useful to distinguish intrinsic spectral features from inhomogeneous «site effects». In the present case, they show that excitation of either of the two distinct absorptions appearing in the isotopically mixed samples produces the same, unshifted emission spectrum, that is that the splitting is homogeneous and both new absorption bands belong to the same molecular species.

A further clue is obtained if one uses the zero-point energy difference discussed above to estimate the upper state asymmetric stretching frequency ν_3'. When a joint fit of the Cu^{16}O$_2$, Cu^{16}O^{18}O, and Cu^{18}O$_2$ isotopic data including the ground state ν_3'' bands discussed in the previous paragraphs is carried out, including the other vibrational modes of CuO$_2$ in the fitting process, with the upper state asymmetric stretch as an adjustable parameter, the systematic errors mentioned above disappear, and one obtains a nearly perfect fit of the data (RMS error < 0.15 cm^{-1}). The unknown upper state ν_3' of the mixed Cu^{16}O^{18}O converges to a value of around 610 cm^{-1}, very close to the expected symmetric stretching frequency. The measured values of ν_1' are 617.13 and 582.08 cm^{-1} in Cu^{16}O$_2$ and Cu^{18}O$_2$, respectively, suggesting that ν_1' and ν_3' modes of the dioxide may have very similar frequencies
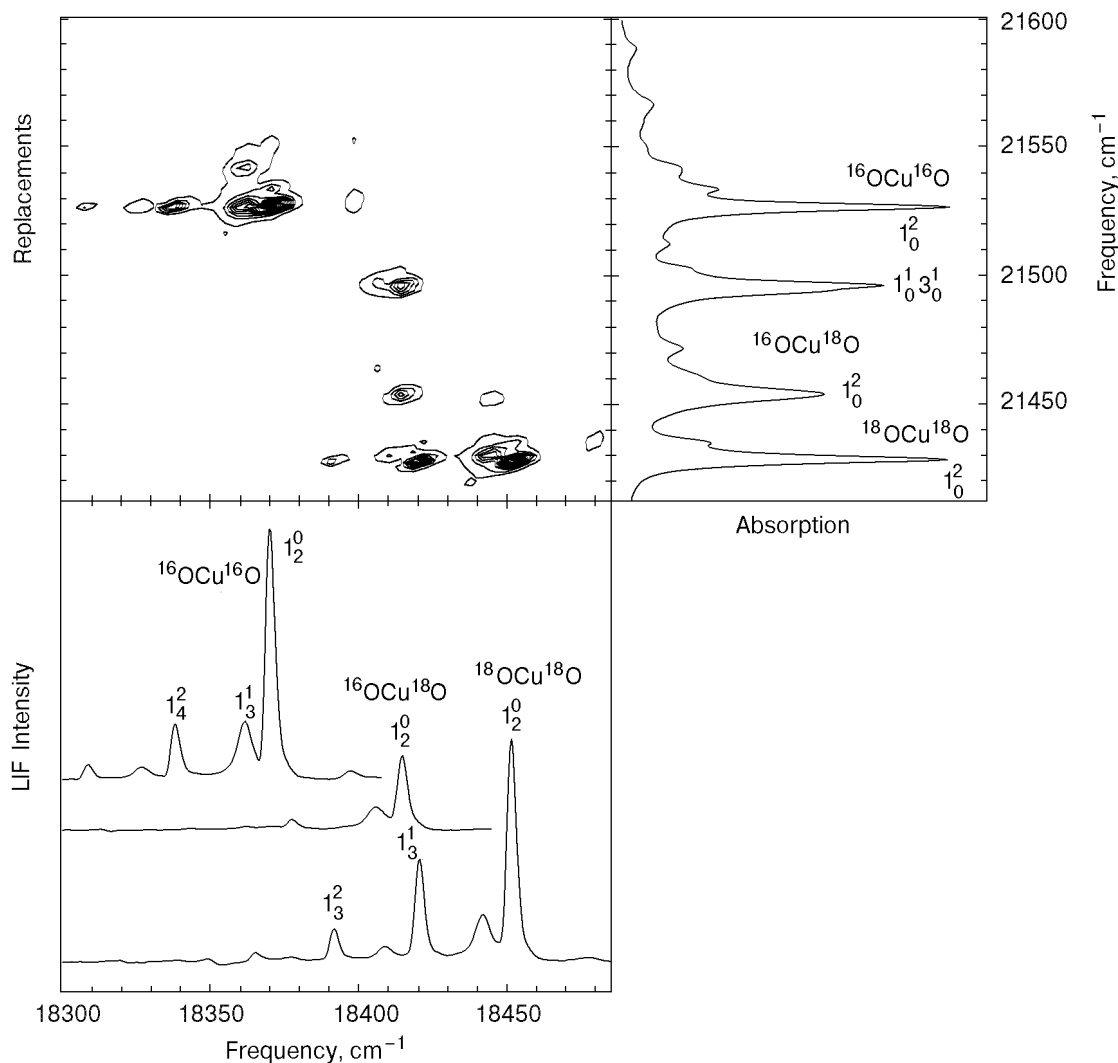
Fig. 4. Part of a 3D spectrum of the different isotopomers of OCuO in solid xenon. The absorption spectrum is plotted along the abscissa, and the three LIF spectra are plotted on the ordinate. The LIF spectra can be seen as a cut trough the 3D spectrum parallel to the ordinate axis.

and that the asymmetric isotopic substitution in $^{16}O^{63}Cu^{18}O$ may result in a strong mixing of the two stretching frequencies.

2.3. Normal mode analysis and vibrational mode mixing in CuO_2

This idea of mixing the nearly isoenergetic (0,0,1) and (1,0,0) upper state levels, which may interact when the symmetry is broken by the asymmetric isotopic substitution, can be tested by normal coordinate analysis [14], which we carried out for both the ground and excited electronic states of CuO_2 using all the available isotopic data. With the values of 661.2, 641.04 and 623.86 cm^{-1} measured for v_1, the symmetric stretching vibration of the three oxygen isotopic species, and the 816.76 and 812.6 cm^{-1} v_3 frequencies observed for the asymmetric $^{16}O^{63}Cu^{18}O$ and $^{16}O^{65}Cu^{18}O$ molecules

in the ground states, one computes a Cu–O stretching force constants of $k_r = 4.219$ mdyn/Å, with a very small interaction force constant $k_{rr} = -0.095$ mdyn/Å. These are somewhat lower than for similar transition metal dioxides like TiO_2 ($k_r = 6.9$ mdyn/Å, $k_{rr} = 1.86$ mdyn/Å) or CrO_2 ($k_r = 6.65$ mdyn/Å, $k_{rr} = 1.21$ mdyn/Å) but still indicative of rather strong, multiple metal–oxygen bonds. Inspection of the normal coordinates indicates that even for the mixed isotopic molecule, $^{16}OCu^{18}O$, the 641.04 cm^{-1} frequency is to a very good approximation a symmetric stretching vibration, involving very little motion of the central copper atom. This normal-mode analysis predicts values of $v_3 \approx 830$ and 799 cm^{-1} for the unobserved asymmetric stretches of the isotopically pure, symmetric $Cu^{16}O_2$ and $Cu^{18}O_2$ molecules, respectively. One also computes for the symmetrical $Cu^{17}O_2$

molecule vibrational frequencies almost identical to those observed for the asymmetrical $^{16}OCu^{18}O$ oxide with the same overall mass.

A similar analysis carried out for the excited electronic state data reveals quite a different situation. Assigning the observed 617.13, 582.08 and 592.42 cm^{-1} frequencies to the ν_1 symmetric stretching mode of the three isotopomers, and the fourth, 625.2 cm^{-1} vibration to ν_3 of $^{16}OCu^{18}O$, one obtains a considerably smaller value for the Cu–O stretching force constant, $k_r = 3.035$ mdyn/Å, with a much larger, positive stretch–stretch interaction force constants $k_{rr} = 0.56$ mdyn/Å. The calculation predicts for the unobserved asymmetric ν_3 modes of $Cu^{16}O_2$ and $Cu^{18}O_2$ values of 628.9 and 605.3 cm^{-1}, indicating that in both isotopic molecules the upper state ν_1 and ν_3 vibrational frequencies are very close, differing by only about 11.6 and 23.2 cm^{-1}, respectively. The asymmetric isotopic substitution results, however, in a strong interaction, with the two levels «repelling» each other. As a result, the splitting of its vibrational frequencies, $\nu_1 = 591.6$ cm^{-1} and $\nu_3 = 625.2$ cm^{-1} increases from the expected value of about 17.4 cm^{-1} — the average of the splitting in the pure isotopic molecules — to 33.6 cm^{-1}. These computed frequencies differ substantially from those obtained for the symmetric $Cu^{17}O_2$ molecule where the interaction is absent. Here the splitting of the computed vibrations $\nu_1 = 616.7$ cm^{-1} and $\nu_3 = 598.75$ cm^{-1} is only 17.9 cm^{-1}, almost exactly intermediate between the $Cu^{16}O_2$ and $Cu^{18}O_2$ values. Analysis of the normal modes of $^{16}OCu^{18}O$ reveals that they resemble more closely a ^{16}O–Cu and Cu–^{18}O vibration, respectively, rather than a symmetric and asymmetric stretch, and both vibrations involve an appreciable motion of the central copper atom. A further consequence of the level mixing is that both the bands observed in the spectrum, nominally (1,0,0) and (0,0,1) in (ν_1', ν_2', ν_3') notation, exhibit a ^{65}Cu–^{63}Cu isotopic splitting. Such strong interactions and breakdown of the selection rules would not be surprising in symmetric hydrides (e.g. HCCD), where the difference of masses is a factor of two, but is fairly uncommon where heavier atoms are involved.

This interaction due to the reduced symmetry of $^{16}OCu^{18}O$ is not restricted to the (1,0,0) and (0,0,1) levels of the excited CuO_2 state, but propagates also to higher levels of vibrational excitation. Thus the (2,0,0) level can — and does — mix with the (1,0,1) and (0,0,2) levels, yielding a group of three absorptions. Similarly (3,0,0), (2,0,1), (1,0,2), and (0,0,3) can interact, and the intensity
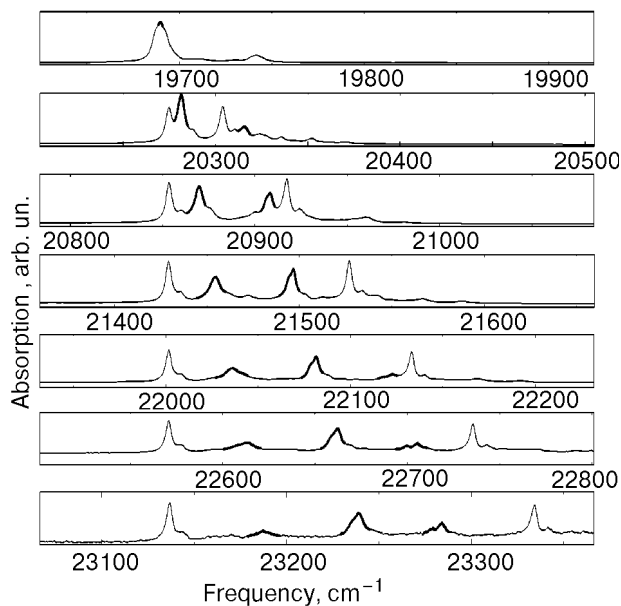

Fig. 5. Absorption spectrum of OCuO, generated from the isotopic mixtures of ^{16}O, $^{16}O^{18}O$ and ^{18}O. The absorption of $^{16}OCu^{18}O$ lies between that of $^{16}OCu^{16}O$ and $^{18}OCu^{18}O$ and is emphasized with a thicker linewidth.

in the mixed molecule is distributed between more and more levels as one proceeds to higher and higher levels of excitation, even though for high values of ν_1' not all of the interacting levels can be identified. The appearance of such interacting multiplets can clearly be observed in the absorption spectrum in Fig. 5. The situation is quite similar to the appearance of «Fermi polyads» in the spectra of many linear molecules exhibiting Fermi resonances, most commonly between the symmetric stretch and the even overtones of the bending vibration.

2.4. Vibrational relaxation and hot fluorescence

Vibrational relaxation in polyatomic molecules is usually fast, and very often only the emission from the vibrationless level of excited electronic states is observed. Unlike the previous studies of CuO_2 in lighter rare-gas matrices where mainly relaxed emission was detected, in the xenon matrix the vibrational relaxation is apparently considerably slower, and a rather intense unrelaxed «hot» fluorescence from upper state levels up to $\nu_1 = 6$ is quite strong and easily observable. At first sight one might perhaps expect stronger guest–host interactions, and consequently faster relaxation in the more polarizable solid xenon, but somewhat surprisingly frequently exactly the opposite trend is observed. One difference is that in the less polarizable neon the guest-host interactions tend to be repulsive, in the looser sites of the larger more polarizable hea-

vier rare gases, and in particular in solid xenon, attractive interactions usually prevail. The molecular vibration against the steep repulsive potential in solid neon or argon may result in a stronger coupling between the molecular vibration and the phonon modes of the lattice. Also classically one might expect a more efficient energy transfer from the light atoms such as oxygen to lattice atoms with a mass comparable to neon, than to the much heavier xenon.

We have examined spectra with an excitation of up to $v_1' = 6$ of the upper state, and a typical spectrum is shown in Fig. 3. It contains sequences of bands corresponding to emission from all the $(v_1',0,0)$ levels up to $v_1' = 6$, with the ground state vibrational progressions extending to $v_1'' \approx 10$. Similar to the relaxed emission, also the hot fluorescence of the asymmetric $^{16}OCu^{18}O$ molecule contains, besides the strong v_1'' progressions, numerous weaker bands missing in the symmetric isotopic species $Cu^{16}O_2$ and $Cu^{18}O_2$. These are transitions of the type $1_n^m 3_1^0$, that is involving one quantum of v_3''. They all show a distinct splitting into two components due to the naturally occurring isotopes ^{63}Cu and ^{65}Cu (abundances 69% and 31%).

It is perhaps useful to note that although intense unrelaxed fluorescence from upper state levels involving v_1' excitation is observed, there is no evidence for emission from levels involving the other modes, v_2' or v_3'. This may be not extremely surprising. The v_2' mode has a much lower frequency than v_1', and based on the energy gap law, one would expect an efficient vibrational relaxation. On the other hand, as discussed in the previous section, the v_3' mode has a higher vibrational frequency than v_1', but lies very close above it. The levels involving the upper state v_3' of the type (v_1, v_2, v_3) will relax efficiently into nearby levels (v_1+1, v_2, v_3-1) just a few wavenumbers below them.

2.5. The ground state bending vibration

Upon close examination the emission spectra of the symmetric species $Cu^{16}O_2$ and $Cu^{18}O_2$ do not only reveal the main v_1'' progressions but also numerous very weak bands, as shown in Fig. 3,a, which are however of a different nature than those observed for the asymmetric $^{16}OCu^{18}O$ molecule, and can clearly not be attributed to the v_3'' vibration. These bands are all shifted approximately $160 cm^{-1}$ from the main v_1'' progression bands, and can be reasonably assigned to transitions of the type $1_n^m 2_1^0$, that is to bands involving one quantum of the ground state bending vibration v_2''. Two interesting observations can however be made. In the

first place, these bands are only observed for $m \geq 1$, that is for hot emission originating from levels involving at least one quantum of v_1'. In the second place, the value of v_2'' implied, $\approx 160 cm^{-1}$, is considerably smaller than the $193 cm^{-1}$ previously measured in solid neon.

The absence of the bands involving the bending from the vibrationally relaxed spectrum is quite conspicuous, the corresponding bands originating from the vibrationless (0,0,0) level must be at least an order of magnitude weaker than the bands from vibrationally excited $(v_1',0,0)$ levels. Strictly speaking, bands involving one quantum of v_2'' are symmetry-forbidden, and should not appear at all in the spectrum of a linear, centrosymmetric CuO_2. One possible explanation would be that the bending potential changes with stretching mode excitation. One could then invoke a small barrier to the linearity of CuO_2, whose height increases with v_1' excitation. The molecule in the vibrationless level would then still be linear, but the hot fluorescence would follow the bent molecule selection rules, with the molecule deviating slightly from linearity in levels with v_1' excitation. The ground state v_2'' frequency also exhibits a large anharmonic interaction constant $x_{12}'' = -6.9 cm^{-1}$. Its medium shift in comparison with neon is rather large, but not unprecedented, and will be discussed in a section dealing with matrix effects.

2.6. The upper state bending vibration and Renner–Teller splitting

Fluorescence excitation spectra typically provide a better signal-to-noise ratio and more details than absorption spectra. If one examines the region between the bands of the main v_1' CuO_2 progression in more detail, numerous weaker bands are again detected. Thus in the $F–X$ excitation spectrum of $Cu^{16}O_2$ one detects a very weak band about $120 cm^{-1}$ above the vibrationless $(v_1' = 0)$ level, then a rather broad doublet at 166 and $185 cm^{-1}$, a sharp weak band at $230.1 cm^{-1}$, and finally a moderately strong band at $342.8 cm^{-1}$. These bands do not form easily recognizable regular progressions, but almost identical patterns are detected above the $v_1' = 1, 2$, and higher levels of the main v_1' progression. Furthermore, in the excitation spectrum of the isotopic $Cu^{18}O_2$ molecule a very similar structure is detected, only the intervals are slightly reduced, in fact almost exactly by the ratio which would be expected for the bending v_2 frequency of CuO_2.

The simplest explanation would be to attribute this complex pattern to a relatively large Renner–Teller splitting of the v_2' vibration in the excited

doublet state, perhaps into components near 115 and 170 cm^{-1}, with the bands near 230 and 340 cm^{-1} being the corresponding overtones. One problem with this interpretation is that would require the excited state to be an orbitally degenerate $^2\Pi$ or possibly a $^2\Delta$ state, while theory seems to predict a $^2\Sigma$ state closest to the excited E-state energy. Nor does this interpretation explain the differences in the shapes of the different bands, and it gives no clue why the two higher energy bands are sharp, while the band near 170 cm^{-1} appears as a doublet and is broadened. A gas phase study of the CuO$_2$ spectra would clearly be very desirable, and necessary to answer this question unambiguously and determine the symmetry of the E-state.

2.7. Lower lying electronic states of CuO$_2$

Already Shirk and Bass in their early experiment noted that in solid argon a new progression of bands seems to begin at 16595 cm^{-1}, and a similar observation was made in a later solid neon LIF study. There was some controversy as to whether this further transition involves emission form the excited E-state into some lower lying electronic state, or if the E-state relaxes nonradiatively into a lower state located at 16595 cm^{-1}, which then fluoresces into the ground state. In our present work we observe not only this progression whose origin is shifted to 15799.6 cm^{-1} is solid xenon, but also an additional one with an even lower energy originating at 13003.5 cm^{-1}. As noted previously, in the xenon matrix vibrational relaxation is slow, and an extensive vibrationally unrelaxed emission from levels with $v' > 0$ is detected. The observed hot fluorescence answers the above controversy unambiguously: depending on which vibrational level of the F-state is excited, all three transitions exhibit the same vibrationally unrelaxed band structure, demonstrating that all the spectra involve emission directly from the excited CuO$_2$ E-state levels into the electronic ground state (X), and into two other, low-lying electronic states. These states which we denote A and B, are located in solid xenon at 3387.3 and 6683.4 cm^{-1} above the X-state, respectively.

Using an infrared germanium detector and extending the spectra to even lower energies, an additional band system near 9500 cm^{-1} is detected. The new spectrum seems to involve at least two progressions of bands with the strongest being located near 8420 cm^{-1}. In solid xenon the bands are rather broad, but even in this case, when higher vibrational levels of the E-state are excited, one observes what appears to be vibrationally unrelaxed emission, suggesting again that emission probably

originates from the E-state, and ends in two further low-lying states D and C at energies near 11270 and 11060 cm^{-1}, respectively. These infrared emissions sharpen appreciably in solid. Specifically for the «b-site» investigated most extensively in the previous neon matrix study they are shifted to 11110.5 and 11309.5 cm^{-1}, respectively.

2.8. Electronic structure of CuO$_2$

The electronic structure of the molecule is surely rather complex, and it is not well understood. Mochizuki et al. in their theoretical investigation of the linear form of CuO$_2$ [11] find some thirty electronic states within the range of energies studied in this work, that is below 25000 cm^{-1}. In agreement with previous suggestions they conclude that the molecule has an $X\,^2\Pi_g$ ground state, and based on population analysis find that, as could be expected, the bonding is considerably more covalent than in CuF$_2$, which can be well represented by the ionic structure F$^-$Cu^{2+}F$^-$. The authors assign the strong visible matrix absorption, referred to as E-state in this work, to the fully allowed transition into the second state of $^2\Sigma_u^+$ symmetry, calculated to lie at 20079 cm^{-1}.

The xenon matrix data provide extensive new information about the CuO$_2$ properties and electronic structure. In addition to the extensively studied E-state, which, in solid xenon, occurs at 19686.9 cm^{-1}, the emission spectra provide evidence for at least four other, lower-lying electronic states, located in the xenon matrix at 3387.3, 6683.4 11060, and 11270 cm^{-1}. The theoretical study mentioned above predicts lowest excited electronic states at 6304 cm^{-1} ($^2\Pi_u$), 7592 cm^{-1} ($^2\Sigma_g^-$), 8365 cm^{-1} ($^2\Delta_g$), and the authors suggested that «the emission band around 3850 cm^{-1}» is due to the $^2\Pi_u \leftrightarrow X\,^2\Pi_g$ transition. This is, however, due to their misunderstanding of the previous experimental data; there is no observed 3850 cm^{-1} emission band in neon, the existence of a state at 3850 cm^{-1} (analogue of the 3387.3 cm^{-1} band in xenon) was inferred from an observed visible emission originating in the E-state ($2\,^2\Sigma_u^+$ based on the Mochizuki et al. assignment [11]). If the E-state emitting in the matrix is indeed $2\,^2\Sigma_u^+$, then all the lower states observed should be of gerade symmetry, an $E\,(2)\,^2\Sigma_u^+ \leftrightarrow\,^2\Pi_u$ emission would naturally be parity-forbidden. Perhaps the 7592 cm^{-1} $^2\Sigma_g^-$ state might be an alternative assignment for the 3387.3 cm^{-1} xenon matrix state. It may also be noted that one often finds $\Pi \leftrightarrow \Pi$ transitions to be more intense than $\Pi \leftrightarrow \Sigma$ ($\Delta\Lambda = \pm 1$), and one of the states of $^2\Pi_u$ symmetry might be an alternative

Table 1

Summary of the OCuO vibronic bands (in cm^{-1}) in different matrices. The parameters were chosen according to the zero-point energy of $^{16}O\,Cu\,^{16}O$

Matrix	Site	X ω_1^0	X ω_2^0	X ω_3^0	A ω_1^0	A ω_2^0	B ω_1^0	C ω_1^0	D ω_1^0	D ω_2^0	E ω_1^0	E ω_2^0	E ω_3^0
Neon	f	655.8											
	a	655.5									608.3		
	b1	661.5									614.5		
	b2	654.7			590 [5]						607.7		
	c	660.3									612.3		
	d	659.7	193.4					640.8	636.8	234	611.5	135.6	
Argon [15]	c	651.6									608.1		
	b	670.4		823.0 [9]							627.5		
	a	668.5									625.9		
Xenon	a	664.2	161.5	830.3	597.8	113	569.7				618.9	118	628
	b	662.7									615.6		
N$_2$		663.8			826.7 [9]						614.1		

candidate for the E-state, since the observed complex bending frequency structure observed in our work would be easier to explain with a $\Lambda > 0$ upper state. In view of the expected large density of low-energy states, confident specific assignments without gas phase rotational analysis are quite difficult.

The CuO$_2$ molecule was recently investigated in the gas phase by means of CuO$_2^-$ photodetachment spectroscopy by Wu et al. [12]. Their work, in addition to establishing an electron affinity of 3.47 eV for the dioxide, also indentified several low-lying electronic states near 2580, 5080, and 6430, 9680, and 13630 cm^{-1}. Except for the 6530 cm^{-1} state, the differences between the photoelectron work and the xenon matrix data seem to lie well outside the combined states error limits of the two works. It is at this point not obvious if different electronic states are involved, if the actual errors are larger than estimated, or if the differences can be explained by the matrix medium effects to be discussed below.

2.9. Molecular constants of CuO$_2$ in xenon

The efficient formation of the oxide, and its high transition moment resulted in high quality spectra, so that overall more than 300 vibronic bands for six different isotopic species of CuO$_2$ in xenon matrix were measured. Part of this data is summarized in Table 1. The observed bands involve, however, mainly the totally symmetric ν_1 vibration. The data for the other vibrational modes are naturally more fragmentary.

Table 2

The vibrational frequencies obtained by a fit not including terms higher than quadratic. The observed ν_1 levels extending up to $v'' = 10$ and $v' = 6$ are reproduced with an error of < 0.2 cm^{-1}. We used the frequencies ν_i directly measured in the experiment, rather than the ω_i constants of the polynomial Dunham type expansion

Isotope	Upper state ν_1	Upper state ν_3	Upper state ν_2	Ground state ν_1	Ground state ν_3	Ground state ν_2
$^{16}O^{63}Cu^{16}O$	617.1		138.1		661.2	190.0
	617.6	629.3	138.0	830.8	661.4	189.9
$^{18}O^{63}Cu^{18}O$	582.1		132.9		623.86	183.6
	582.4	605.7	132.9	799.7	623.98	183.4
$^{16}O^{63}Cu^{18}O$	592.4	625.5		816.9	641.1	
	592.0	625.7	135.5	816.8	641.0	186.4
$^{16}O^{65}Cu^{18}O$	591.5	623.9		812.6	641.0	
	591.0	623.2	134.8	812.6	640.9	185.4
$^{17}O^{63}Cu^{17}O$						
	599.3	616.9	135.4	814.5	641.8	186.2

Table 2 shows the spectroscopic constants obtained by a global fit of the observed transitions, using the appropriate isotopic relationships for the data of the isotopic molecules. The ν_1 potential in both the E- and X-states is well approximated by a Morse potential. Without including terms higher than quadratic, the observed ν_1 levels extending up to $\nu'' = 10$ and $\nu' = 6$ are reproduced with an error of < 0.2 cm^{-1}. In the table we give the vibrational frequencies ν_i directly measured in the experiment, rather than the ω_i constants of the polynominal Dunham type expansion. The latter have the disadvantage to depend on the inter-mode coupling and change whenever an additional anharmonic constant is included. Besides the fundamental frequencies, also a number of the anharmonic x_{ii} constants could be established. Interesting are the uncommonly large values of the inter-mode coupling constants x''_{12} and x''_{13}.

2.10. Medium effects

Since CuO_2 was now examined in all rare gases and also in solid nitrogen, it is of interest to comment on the medium induced shifts and changes in its molecular constants and properties which are, as previously noted, unusually large. The molecule occurs in all matrices in several different sites, but if the most populous site in each matrix is considered, the T_e value of the E-state shifts from 20700 cm^{-1} in solid neon to 20486.5, 20064 and 19686.9 cm^{-1} in solid argon, krypton and xenon. Such a shift of more than 1000 cm^{-1} or 5% is considerably larger than typically observed. Even more remarkable are the large shifts between different sites in the same matrix. Thus the T_e values in six different sites in neon span an energy range of 163 cm^{-1}, while three sites in argon are spread over 223 cm^{-1}. One usually observes large matrix shifts for molecular ions, or highly polar compounds. Naturally linear centrosymmetric CuO_2 has no dipole, but the compound is very likely to be quite ionic, with highly polar Cu—O bonds, which might explain the large effects.

Interestingly, the lower states for which data are available, A, C, and D seem to exhibit much smaller shifts of more typical magnitudes. For example, comparing the most studied sites in neon and xenon, the $D-X$ transition shifts from 11309.5 to 11268.5 cm^{-1}, a shift of 41 cm^{-1}, while the $E-X$ transition at less then twice the overall energy exhibits a shift of more than 1000 cm^{-1}. In general, one usually observes particularly minor shifts between two or more states which arise from the same, or a very similar electronic configuration.

Besides large electronic shifts, CuO_2 also experiences unusually large shifts in the excited E-state vibrational frequencies. Thus in neon the ν'_1 frequency ranges from 607.7 to 614.5 cm^{-1}. In argon the reddest «c» site has a ν'_1 value of 608.1 cm^{-1}, well within the neon range, while in two «bluer» sites it shifts drastically to 627.5 and 625.9 cm^{-1}, a change of more than 3%. In solid krypton and xenon the ν_1 then gradually returns back to lower frequencies. A possible interpretation would be that there are two types of sites, one appearing only in neon and argon, and another yielding strongly blue-shifted vibrational frequencies. The latter site occurs in all the heavier rare gases, it is only in argon that both types of sites are present — perhaps double and triple substitution sites.

Unusual is also the behavior of the formally forbidden bending modes which appear weakly in the matrix spectra and which, based on the limited data, undergo particularly large medium-induced frequency changes. The ν''_2 seems to decrease from 196 cm^{-1} in solid neon to the ≈ 160 cm^{-1} value observed in xenon, an almost 20% shift. It is, however, a common experience that low-frequency bending modes are most likely to be affected by the condensed medium. An extreme example is the ν''_2 frequency of C_3 which changes from 63 cm^{-1} in the gas phase to 84 cm^{-1} is solid argon, a more than 25% shift. Such changes are caused on the one hand by the resistance of the host matrix to bending of the guest, but are also due to partial charge transfer from the rare gas to the molecular orbitals of the guest, increasing (or decreasing) its rigidity. The ability of the matrix to donate electrons will naturally correlate with the polarizability and ionization potential of the matrix atoms, but also depend sensitively on the specific nature and geometry of the matrix site. Charge transfer interactions may be particularly significant for strongly polar or ionic compounds such as CuO_2, and this might explain the unusually large medium effects observed.

Summary

We investigated optical absorption and laser induced fluorescence spectra of CuO_2 in several solid matrices. We found several new electronic states determined their vibrational frequencies. The matrix data are compared with the results of recent gas phase CuO_2^- photodetachment studies, and with ab initio calculations. We found and discussed the unusually large matrix effects and medium-induced electronic and vibrational frequency shifts for this molecule.

1. J. S. Shirk and A. M. Bass, *J. Chem. Phys.* **52**, 1894 (1970).

2. M. J. Griffiths and R. F. Barrow, *J. Chem. Soc. Faraday Trans.* **273**, 943 (1977).

3. H. M. Rojhantalab, L. Allamandola, and J. Nibler, *Ber. Bunsenges. Phys. Chem.* **82**, 107 (1978).

4. D. E. Tevault, *J. Chem. Phys.* **76**, 2859 (1982).

5. V. E. Bondybey and J. H. English, *J. Phys. Chem.* **88**, 2247 (1984).

6. J. Hrusák, W. Koch, and H. Schwarz, *J. Chem. Phys.* **101**, 3898 (1994).

7. H. P. C. W. Bauschlicher, S. R. Langhoff, and M. Sodupe, *J. Phys. Chem.* **97**, 856 (1993).

8. T. K. Ha and M. T. Nguyen, *J. Phys. Chem.* **89**, 5569 (1985).

9. G. V. Chertihin, L. Andrews, J. Charles, and W. Bauschlicher, *J. Phys. Chem.* **A101**, 4026 (1997).

10. Y. Mochizuki, U. Nagashima, S. Yamamoto, and H. Kashiwagi, *Chem. Phys. Lett.* **164**, 224 (1989).

11. Y. Mochizuki, K. Tanaka, and H. Kashiwagi, *Chem. Phys.* **151**, 11 (1991).

12. H. Wu, S. R. Desai, and L.-S. Wang, *J. Chem. Phys.* **103**, 4363 (1995).

13. H. Wu, S. R. Desai, and L.-S. Wang, *J. Phys. Chem.* **A101**, 2103 (1997).

14. P. R. Stannard, M. L. Elert, and W. M. Gelbart, *J. Chem. Phys.* **74**, 6050 (1981).

15. A. Lammers, *Fourier-Transform-Spektroskopie von* Tl *und* CuO$_2$ *in Edelgasmatrizen. Diplomarbeit*, Master's thesis, Institut für Physikalische und Theoretische Chemie der Technischen Universität München, 1994.