

17 July 1998

Chemical Physics Letters 291 (1998) 291-299

CHEMICAL PHYSICS LETTERS

Relaxation and vibrational fluorescence of WO in solid neon

Martin Lorenz, Jürgen Agreiter, Nicola Caspary, Vladimir E. Bondybey *

Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstraße 4, D-85748 Garching, Germany

Received 28 April 1998

Abstract

Studies of laser-induced fluorescence of tungsten oxides in solid neon at 6 K provide interesting insights into the mechanisms of WO relaxation. The relaxation occurs by interelectronic cascade between the vibrational manifolds of excited electronic states, eventually reaching the v'' = 7 of the ground electronic state. Remarkably, for the heavy WO oxide, the non-radiative processes are surprisingly inefficient, with relaxation in the ground state apparently occurring predominantly by sequential vibrational fluorescence. The relaxation pathways of WO are discussed and compared with relaxation in lighter, first-row molecules exemplified by CN. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Low-temperature rare-gas solids are a useful medium for studies of molecular relaxation and non-radiative processes [1-4]. While relaxation in the condensed phase is usually fast, often proceeding on a picosecond or even subpicosecond timescale, at low temperatures in solid rare gases it often slows down remarkably. In small molecules often vibrationally unrelaxed 'hot' electronic fluorescence is observed and in particular in the ground states of light molecules the non-radiative relaxation may be slow. In a number of light molecules, mostly involving hydrides or simple compounds of first-row elements, vibrational fluorescence was also observed and investigated [5-10]. The diatomic CN is an example of a molecule which exhibits a slow relax-

* Corresponding author.

E-mail: bondybey@verona.phys.chemie.tu-muenchen.de

ation and for which intense vibrational fluorescence is observed [11].

Relaxation for molecules involving heavier elements is usually efficient, and even in electronic spectra one mostly sees only vibrationally relaxed fluorescence or phosphorescence. Particularly in transition metals, with their dense manifold of electronic states, fast relaxation is usually the rule and only in relatively few cases extensive 'hot' fluorescence is detected. We have recently examined the spectroscopy and photophysics of the oxides of the third-row transition metal tungsten [12]. Rather surprisingly we have observed that, in spite of the essential differences between the two molecules, the energy relaxation in WO parallels the processes previously detected in CN [13,14]. Extensive vibrationally unrelaxed emission from several electronic states is observed and even more surprisingly, quite intense ground-state vibrational fluorescence is easily detectable. Our observations of the WO relaxation behavior are the subject of this Letter.

^{0009-2614/98/\$19.00 © 1998} Elsevier Science B.V. All rights reserved. PII: S0009-2614(98)00605-8

2. Experimental

Tungsten and its oxides are high-melting refractory materials and their vaporization requires temperatures ranging up to 3000 K. Here we employ a technique developed in our laboratory more than a decade ago [15]: laser vaporization of the metal in the presence of a large excess of cold carrier gas. neon gas being used to grow the matrix. The frequency-doubled pulses of an Nd-YAG laser (30 mJ) used to vaporize a tungsten target are synchronized with the opening of a fast valve admitting pulses of the carrier gas. The valve, with opening times of 0.1ms, is operated with a backing pressure of 5 bar of a 500:1 mixture of neon with O_2 (or ${}^{18}O_2$). The neon gas with the products and oxides formed in the vaporization fixture are then condensed on a 6 K silver-coated copper substrate.

The deposits are examined spectroscopically with the help of a Bruker IFS 120 HR FT instrument with a spectral range from 500 to 30000 cm⁻¹. Spectra have been recorded with resolutions of 0.5 cm⁻¹ and 0.06 cm^{-1} (IR). To excite the sample fluorescence, either an argon ion laser pumped dye laser, or a Ti-Sapphire laser were used. A PMT detector was used in the visible and UV range, while germanium and indium antimonide detectors were available for studies in the near infrared range.

3. Results and discussion

3.1. WO electronic structure

Tungsten oxides were studied in solid rare gases more than 30 years ago by Weltner and McLeod [16], who observed a number of WO electronic states in the visible region, and some of these states were some 10 years later also investigated by Samoilova et al. in the gas phase [17]. Nelin and Bauschlicher have more recently investigated WO by ab initio techniques, which suggested that the ground state is formally a ⁵II state and predicted the excited ⁵ Σ and ⁷ Σ states in the visible region. Their calculations yielded another, low lying ⁷II state around 7400 cm⁻¹ in the near infrared [18]. The electronic structure of transition metals and the ability of ab initio methods to predict it is a topic of considerable current interest and we have therefore decided to re-examine the WO spectroscopy using absorption and fluorescence techniques, in order to gain additional spectral information and characterize possible transitions in the infrared.

The solid neon matrices, generated by laser vaporizing tungsten in the presence of a small amount of oxygen, contained diatomic tungsten oxide, as evidenced by infrared absorptions. Not only the oxygen, but also the tungsten isotopes are clearly resolved. Thus absorptions due to ${}^{184}W^{16}O$ and ${}^{184}W^{18}O$ occur at 1056.49 and 1001.25 cm^{-1} , respectively. In agreement with Weltner and McLeod, we observe in the visible the states he denotes A-F, as well as several new states. In addition, in the near infrared we have detected a group of states. Several progressions occur with origins between 7403.8 and 8007.6 cm⁻¹, with by far the strongest ν_{00} absorption occurring at 7527.76 cm⁻¹ (7529.08 cm⁻¹ for W¹⁸O). While some of the weaker bands appearing here are due to WO in 'perturbed' matrix sites, there are clearly at least three absorbing states present in this region. They may be components of the $^{7}\Pi$ state predicted by Nelin and Bauschlicher. We will report

Table 1 Molecular constants of ¹⁸⁴W¹⁶O in solid neon

State ^a	$T_{\rm e}$ (cm ⁻¹)	$\omega_{\rm e}$ (cm ⁻¹)	$\omega_{\rm e} x_{\rm e}$ (cm ⁻¹)
Х ⁵ П	0.0	1064.49	3.998 ^b
$a(^{7}\Pi?, \text{ red site})^{c}$	7454.3	957.9	3.27
a(⁷ ∏?) ^c	7578.6	959.6	3.76
b(⁷ П?) ^с	7761.1	958.7	3.55
с(⁷ П?) ^с	8062.1	956.1	3.26
d ^c	10938.7	1022.3	
e ^c	12075.4	970.5	
f ^c	14132.7	1084.3	
$A(^{5}\Sigma \text{ or }^{7}\Sigma?)$	14116.9	1051.2	10.84
В	17336.9	929.5	-1.07
C	19267.5	932.6	2.76
D (red site)	20799.8	996.8	8.22
D	20821.4	998.7	8.51
Е	21538.2	971.3	8.49
F	23439.4	955.4	9.52
G	23852.7	934.2	-5.1
H' ^{c,d}	27037.3	931.6	13.15

^aSymmetries as proposed by Nelin and Bauschlicher [18].

 ${}^{b}\omega_{e} y_{e} = -0.0034 \text{ cm}^{-1}$ and for the X⁵ Π ground state.

^c Previously not observed.

^dNot identical with the H-state ($T_{00} = 30446 \text{ cm}^{-1}$) of Samoilova et al. [17].



Fig. 1. $W^{16}O$ potential curves and vibrational levels in the range of 0–22000 cm⁻¹. The r_es are obtained by Franck–Condon analysis or are taken, where available, from Samoilova et al. [17].

the details of our spectroscopic observations elsewhere [12] and the present Letter will focus mainly on the WO electronic and vibrational relaxation. We summarize the information about the observed electronic states and their molecular constants necessary for discussing the relaxation processes in Table 1 and show the energy level structure of WO schematically in Fig. 1.

3.2. Fluorescence and relaxation of the excited WO electronic states in the visible

Fluorescence spectra can often provide a valuable complementary contribution to absorption studies. As explained in the experimental section, we have used our tunable laser sources to excite the neon matrix absorptions due to WO. Such an excitation at a variety of frequencies ranging from about 10000 to 25000 cm^{-1} resulted in a fairly strong visible and near infrared fluorescence, whose intensity and spectral distribution depended sensitively upon the excitation wavelength and upon the isotopic species excited. While some levels were emitting efficiently,

others were conspicuously absent, indicative of a complex isotopically dependent pattern of relaxation. This relaxation process is quite complex and involves vibrational manifolds of the numerous electronic states present in this region, both those observed in absorption, and probably of other, 'dark' states. Rates of such interelectronic relaxation processes are known to depend sensitively upon the quantum mechanical coupling between the different electronic states, but also on the 'energy gap' between the relaxing levels and are often governed by the presence of accidental resonances or near resonances.

When the lower energy levels at the red end of the spectrum reported by Weltner and McLeod are excited, the fluorescence is relatively simple and easy to understand. Thus exciting the sample in the v = 0 level of the W¹⁸O in the B-state of Weltner and McLeod at 17273.9 cm⁻¹, one observes emission from the excited level into v'' = 0. 1 and 2 levels of the ground electronic state. A further progression originating from a level at 16980.4 cm⁻¹ into the v'' = 1-4 ground-state levels can also easily be identified as being due to the v' = 3 A-state level, 293.5 cm^{-1} lower in energy. The 16980.44 cm^{-1} is also seen weakly in absorption, although not previously observed by Weltner and McLeod. Excitation of the corresponding v' = 0 B-state level of W¹⁶O $(17280.5 \text{ cm}^{-1})$, on the other hand, produces almost no B-state emission, but mainly weak emissions from the v' = 3 and 2 A-state levels. Owing to the isotopic shift, in the $W^{16}O$ the v' = 3 A-level is only 150 cm⁻¹ below the v' = 0 B-level and the smaller energy gap results in a more efficient depopulation of the B-state.

As one proceeds towards higher energies, the fluorescence gets progressively more complex. For instance, excitation of the v' = 2 D (22635.9 cm⁻¹), produces not only a weak resonant emission from the excited level, but extensive relaxed fluorescence from a number of other levels. No emission is seen from v' = 1 D, but several bands originating from v' = 0 E (21493.0 cm⁻¹) and a fairly strong progression from v' = 0 D (20789.3 cm⁻¹) and a weaker one from v' = 0 B (17274.1 cm⁻¹) are seen. Another rather long progression originates from the A v' = 6 level (19675.5 cm⁻¹) and extends down to 11867.9 cm⁻¹ into the v'' = 8 ground state. In addition to the

clearly identifiable progressions, numerous very weak, sharp bands are observed confirming that in addition to states previously detected by Weltner and McLeod, several other 'dark' or very weakly absorbing states must be present in this region and participate in the relaxation process.

It may be noted that some weak bands appearing in the absorption spectrum are due to 'site effects'. The bands due to 'sites' are, however, easily identified, since unlike excitation of WO in the 'main' site, their excitation results in spectrally shifted emission bands. Thus all the bands of the D progression exhibit a much weaker satellite some 24 cm⁻¹ lower in energy, whose excitation produces fluorescence bands uniformly shifted by the same 24 cm⁻¹.

3.3. Infrared phosphorescence

When the visible bands are excited, one observes not only visible fluorescence, but also a strong emission in the near infrared range, clearly due to the band system also observed in absorption. Representative spectra obtained with the Ge detector by tuning the exciting laser to the B–X 0–0 transition at 17281 and 17274 cm⁻¹ for W¹⁶O and W¹⁸O, respectively, are shown in Fig. 2. Unlike the visible fluorescence,

the emission appearance is essentially independent of which of the vibronic bands of the visible or near IR progressions is excited by the laser and from the multiple 'systems' detected in the absorption spectrum, only the strongest one with its origin at 7527.6 cm^{-1} appears. As already noted above, it may be due to the 'spin forbidden' phosphorescence from the ⁷ Π state, although Λ is probably not well defined in a molecule as heavy as WO. In contrast with the visible fluorescence, the near infrared emission is relatively simple and easy to analyse to yield the molecular constants of the 'a'-state. Interestingly, the infrared spectrum is at least one order of magnitude more intense in the heavier $W^{18}O$ isotopic molecule. which appears with appreciable intensity even in the natural isotopic abundance samples.

The spectra show that vibrational relaxation of WO in neon is relatively slow even in the electronically excited 'a'-state, since not only v' = 0, but also emission originating from vibrationally unrelaxed levels is observed. In the case of the stronger W¹⁸O fluorescence, levels up to v' = 3 are detected in emission and the spectra can be followed with an InSb detector down to about 3300 cm⁻¹ in the infrared, with the progressions in the ground-state



Fig. 2. NIR absorption and phosphorescence of tungsten oxide. The upper trace shows progressions of several NIR states, with the strongest absorption, denoted $a(^7\Pi?) \leftarrow X^5\Pi$, occurring at $T_{00} = 7527.8 \text{ cm}^{-1}$. The lower two traces display the phosphorescence originating from the 'a' ($^7\Pi$?) state of both tungsten oxides, obtained after excitation of the B v = 0 state.

vibrational frequency extending to v'' = 5. The relaxation of the lighter W¹⁶O is apparently more efficient and the corresponding emission appreciably weaker. In this case, besides the vibrationless level only v' = 1 emission is observed.

3.4. Vibrational fluorescence of WO

At the red end of the spectrum obtained with the indium antimonide detector one can observe, starting at around 3000 cm⁻¹, a slowly rising background, which reaches a maximum near 1900 cm^{-1} and then drops to zero due to a cutoff of the InSb detector (see Fig. 3). This broad maximum is clearly due to the high energy end of the 'black-body' radiation from the room temperature apparatus walls. Superimposed over this maximum one can see in the experiment employing natural abundance oxygen three strong absorptions at 2312.4, 2330.6 and 2347.4 cm^{-1} , as well as a group of eight moderately strong emission bands at 1991.5, 2007.8, 2024.1, 2040.4, 2056.6, 2072.7, 2088.8 and 2104.9 cm⁻¹. The three absorption bands are clearly due to three isotopic species of carbon dioxide, C¹⁸O₂, ¹⁶OC¹⁸O and $C^{16}O_2$ probably formed due to the oxygen reaction with a minor carbon impurity in the tungsten target.

The emission bands are readily identified as vibrational overtone fluorescence of diatomic WO, with the eight strong bands being the 9–7, 8–6, 7–5, 6–4, 5–3, 4–2, 3–1 and 2–0 transitions and in addition also the very weak 10–8 bands are detected. This assignment is quite unambiguous and is further confirmed by the clearly resolved tungsten isotopic structure. In an experiment with 18-oxygen, the appropriately shifted 7–5, 6–4, ..., 2–0 bands are observed. A careful examination of the region around 3000 cm⁻¹ revealed also the $\Delta v = 3$ sequence. Finally, as one can see in Fig. 4, the $\Delta v = 1$ transitions could easily be observed between 1000 and 1100 cm⁻¹ using a mercurv–cadmium telluride detector.

As noted above, the visible bands of WO exhibit, in agreement with Weltner and McLeod, strong interstate interactions and perturbations, so that only the W¹⁸O spectrum can be reasonably fitted to obtain the spectroscopic constants of the excited states. However, employing the appropriate isotopic relationships, the ground-state vibrational data including some 80 transitions for eight different isotopic species of WO and involving levels up to v'' = 9, can be almost perfectly fitted. A Morse potential with $\omega_e =$ 1064.65 cm⁻¹ and $\omega_e x_e = 4.046$ cm⁻¹ (for the ¹⁸⁴W¹⁶O isotopomer) reproduces the observed levels



Fig. 3. Vibrational overtone fluorescence of W¹⁶O. The main trace displays the $\Delta v = 2$ and the weaker $\Delta v = 3$ transitions of ground state W¹⁶O in solid neon. Superposed by black-body radiation, the 9–7, 8–6, ..., 2–0 bands are easily observed. The 8–5, 7–4, 6–3 and 5–2 transitions appear near 3000 cm⁻¹, with about one order of magnitude weaker intensity. The insert shows the strong 8–6 transition with tungsten isotopical resolution. Peaks denoted with an asterisk are probably due to impurities.



Fig. 4. Vibrational fluorescence of tungsten oxide in neon. These two graphs show the $\Delta v = 1$ ground-state emission of W¹⁶O and W¹⁸O after excitation at B v = 0. The spectra, measured with a mercury cadmium telluride detector, are background corrected by subtracting the dominating black-body radiation.

with a RMS deviation of $< 0.09 \text{ cm}^{-1}$. While a somewhat better fit (RMS $< 0.03 \text{ cm}^{-1}$) is obtained with $\omega_e y_e = -0.0034 \text{ cm}^{-1}$ (the other constants change slightly to $\omega_e = 1064.49 \text{ cm}^{-1}$ and $\omega_e x_e = 3.998 \text{ cm}^{-1}$), the inclusion of $\omega_e z_e$ or higher terms results in no further improvement.

3.5. X-state vibrational relaxation of WO

The observation of ground-state vibrational fluorescence of WO is rather surprising for at least two reasons. In the first place, while one occasionally observes vibrationally unrelaxed fluorescence in electronic transitions of similar matrix isolated small metal containing molecules, such observations in the infrared are quite uncommon. In view of the much lower oscillator strengths and longer radiative lifetimes associated with vibrational transitions, vibrational fluorescence is usually observed only for hydrides and light molecules involving first row atoms, with high vibrational frequencies usually above 1500-2000 cm⁻¹. In the second place, the groundstate potential of WO is relatively harmonic and therefore one might not expect strong overtone transitions.

Unfortunately, we are not equipped for the direct

measurement of the vibrational lifetimes. Estimating absolute emission quantum yields is always difficult, but semiquantitative consideration of the observed band intensities suggests that it is high and that for every excited molecule several IR photons may be emitted. Such a high quantum yield of vibrational emission indicates that the non-radiative relaxation of the WO ground-state vibrational levels must be exceedingly slow. The fact that life times are long in the WO case is, however, also demonstrated by the fact that absorptions originating in excited vibrational levels can easily be detected. An inefficient energy transfer between the light neon atoms and the much heavier WO molecule might be a contributing factor. In many molecules where strong vibrational fluorescence is observed, e.g. OH, NH, CH₂F or hydrogen halides, it has been demonstrated that the relaxation involves a V-R process, with the rotational modes of the guest molecule being the primary acceptors of the vibrational energy [19]. The rotational constants of WO are much smaller ($B_e \approx 0.415$ cm^{-1}) and the rotations probably contribute little, since high rotational levels would have to be involved.

The appearance of the overtones in the vibrational spectrum will, of course, be aided by the ν^4 dependence of the coefficient of spontaneous emission,

which will favor the $\Delta v = 2$ and 3 transitions by factors of 16 and 81, respectively, and thus counteract the harmonic oscillator selection rules. Even though the mechanical anharmonicity of WO is small, the overtones can be favored by electric anharmonicity. The WO molecule may be fairly ionic, but at larger distances it dissociates into neutral atoms and its dipole is surely not a linear function of r.

The observed relaxation processes, where absorption of a single visible photon is followed by emission of a series of IR photons seems thus far to be unique. It may be noted that similar processes, that is UV pumping, followed by an internal conversion and ground-state vibrational fluorescence are thought to be responsible for the so-called unidentified infrared emission bands (UIE), with polycyclic aromatic hydrocarbons (PAH) being the suggested carriers [20.21]. The search for emission of these species in a neon matrix might be of interest. The excellent signal to noise ratio and clearly high quantum yields of infrared fluorescence observed in WO raise the question if such a behavior might not be much more widespread, and if studies of vibrational emission could not provide a useful general tool for characterizing small metal oxides, carbides or nitrides.

3.6. Pathways of relaxation of WO in solid neon

One of the molecules for which strong infrared emission has been detected, and whose relaxation in matrices has been most extensively investigated is probably the CN radical. Even though the properties and electronic structures of the two molecules could hardly be much more different and while WO has a vibrational frequency about half of that of CN, the relaxation pathways of the two molecules in the matrix are remarkably similar. In the higher energy region, the relaxation proceeds in both molecules by an interelectronic process involving the vibrational manifolds of several excited electronic states. Thus as in CN, the excitation zig-zags between the $B^2\Sigma$ and $A^2\Pi$ electronic states [14], also WO cris-crosses in the visible between the several electronic states available at that energy. The non-radiative interelectronic transitions are dominated by accidental level degeneracies and the rates are governed by Franck-Condon factors and the energy gap law.

When the lowest excited electronic state, the $A^2\Pi$

state in the CN or the 'a' WO state is reached, the process slows down further and in both molecules extensive vibrationally unrelaxed, 'hot' emission, is observed [13]. In CN it was shown that rather than proceeding directly down the vibrational manifold of the A-state, further relaxation occurs exclusively by repeated crossings between the vibrational levels of the $A^2\Pi$ state and the nearest $X^2\Sigma$ ground-state levels. Similarly it is almost certain that also in the lowest a $(^{7}\Pi)$ excited state of WO, the relaxation proceeds by an interelectronic mechanism. In the light CN molecule, the $A^2\Pi$ spin-orbit constant is relatively small (A = -52.64 cm⁻¹), with relaxation between the components being extremely fast and the splitting has little effect upon the relaxation in the matrix. While in WO the spin-orbit effects are surely much larger and the components of the widely separated 'septet' state could be involved in the relaxation, it appears likely that here ground-state levels are involved, too.

After the relaxation reaches the vibrationless v' =0 level of the lowest electronically excited state, only one intramolecular non-radiative process is possible: crossing into one of the nearby ground-state levels. From that point on, the interelectronic channel is closed and the molecule can only relax intrastate, either non-radiatively, or by emitting infrared photons. Thus in the case of CN, the $v'' = 4 X^2 \Sigma$ ground-state level is populated from $v' = 0 A^2 \Pi$. Further relaxation proceeds by sequential infrared fluorescence and the ground-state v'' = 1-4 levels appear strongly in emission. In W¹⁸O the vibrationless v' = 0 a($^{7}\Pi$?) level occurs 7529.39 cm $^{-1}$ above the X v'' = 0 level, with the nearest ground-state vibrational level being at 6857.7 cm^{-1} , 671.69 cm^{-1} lower in energy. Quite analogous to the CN relaxation, as discussed above, the highest level from which vibrational infrared fluorescence is observed is v'' = 7. Clearly also here further relaxation apparently occurs by sequential vibrational fluorescence.

As noted above, in contrast with the heavier isotope, in $W^{16}O$ the a-state emission is weaker and conversely, the vibrational emission considerably more efficient. An explanation is easily found by examining the vibrational level structures of the two oxygen isotopic species, which also provides further support for the relaxation in the lowest a (⁷II?) state proceeding, as in CN, via the ground-state vibra-

tional levels. While in $W^{18}O$, the v' = 0-3 are located 671, 623, 576 and 526 cm⁻¹ above the closest ground-state level, for $W^{16}O$ the numbers are 300, 252, 205 and 158 cm⁻¹ (see Fig. 1). The smaller energy gaps in $W^{16}O$ result in a much more efficient relaxation into the ground-state vibrational manifold, while conversely the larger gaps in $W^{18}O$ lead to enhanced phosphorescence, bypassing the excited ground-state levels.

The involvement of the ground state in a-state relaxation is then directly evidenced by the observation of emission from levels above v' = 0 a $(^7\Pi ?)$. As noted above, also v' = 8, 9 and very weakly also v' = 10 X-levels, located 779, 740 and 701 cm⁻¹ above the v' = 2, 1 and 0 a-state levels, are seen in emission in $W^{16}O$. These relatively large 'energy gaps', combined with poor Franck-Condon factors. make the reverse transition into the a-state once the crossing into the X-state has occurred inefficient and vibrational emission becomes competitive. On the other hand, in the heavier isotope the corresponding gaps are only 360, 320 and 280 cm^{-1} , respectively. This makes the reverse crossing into the a-state more efficient compared with direct sequential radiative vibrational relaxation within the ground state.

3.7. Intrastate vs. interstate vibrational relaxation

As described above, the relaxation in the quite dissimilar molecules CN and WO proceeds in both cases via the same interelectronic mechanism, and similar observations have been made for a variety of other systems. In fact, even when the energy gaps for the two processes are comparable, the interstate process is in general much more efficient. As explained previously, the physical reasons are to be found in Franck-Condon arguments applied to the local phonon modes and to the response of the lattice to the change of state of the guest. The nearby lattice atoms experience little change when the guest molecule changes its vibrational state. This is evidenced by the vibrational spectra of the guest molecules, which mostly exhibit only strong 'zero phonon lines' and little evidence of phonon sidebands.

On the other hand, the electron density distribution in the neighborhood of the guest molecule changes much more drastically when an electronic transition takes place, for instance from a Σ - to a Π -state. This again is usually evidenced by the much more prominent phonon sidebands associated with electronic transitions. Thus in the optical $A^2 \Pi \Leftrightarrow X^2 \Sigma$ transition in matrices, rather strong phonon sidebands are observable. In the case of WO, the phonon wings are weaker, but clearly observable. These same Franck Condon factors which channel energy into the lattice phonons during an optical transition between the two electronic states also facilitate the corresponding non-radiative relaxation process.

4. Conclusion

Pathways of relaxation of electronically excited WO molecules in solid neon at 6 K were investigated. In spite of the much lower vibrational frequency and entirely dissimilar molecular properties and structure, the pattern of relaxation processes resembles those found in the much lighter CN radical. The relaxation occurs by interelectronic cascade between the vibrational manifolds of excited electronic states, reaching eventually the v'' = 7 of the ground electronic state. The non-radiative processes in the ground state are surprisingly inefficient, with relaxation occurring predominantly by sequential vibrational fluorescence.

Acknowledgements

Financial support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. The authors are also indebted to NATO (Grant No. CRG 960009) for additional support.

References

- M. Berkowitz, R.B. Gerber, Chem. Phys. Lett. 49 (1977) 260.
- [2] F. Legay, Chem. Biochem. Appl. Lasers 2 (1977) 43-86.
- [3] H. Kono, S.H. Lin, J. Chem. Phys. 79 (1983) 2748.

- [4] V.E. Bondybey, L.E. Brus, Adv. Chem. Phys. 41 (1980) 269.
- [5] P.F. Zittel, C.B. Moore, J. Chem. Phys. 59 (1973) 6636.
- [6] V.E. Bondybey, L.E. Brus, J. Chem. Phys. 63 (1975) 794.
- [7] C. Blindauer, M. Winter, O. Sild, G. Jansen, B.A. Hess, U. Schurath, J. Phys. Chem. 97 (1993) 10002.
- [8] N. Caspary, B.E. Wurfel, A.M. Smith, V.E. Bondybey, Chem. Phys. 220 (1997) 241.
- [9] H. Dubost, R. Charneau, Chem. Phys. 12 (1976) 407.
- [10] L. Abouaf-Marguin, B. Gauthier-Roy, J. Dupre, C. Meyer, J. Mol. Spectrosc. 110 (1985) 347.
- [11] B.E. Wurfel, G. Schallmoser, G.M. Lask, J. Agreiter, A. Thoma, R. Schlachta, V.E. Bondybey, Chem. Phys. 174 (1993) 255.
- [12] M. Lorenz, V.E. Bondybey, manuscript in preparation.

- [13] V.E. Bondybey, A. Nitzan, Phys. Rev. Lett. 38 (1977) 889.
- [14] D.H. Katayama, T.A. Miller, V.E. Bondybey, J. Chem. Phys. 71 (1979) 1662.
- [15] V.E. Bondybey, J.H. English, J. Chem. Phys. 74 (1981) 6978.
- [16] W. Weltner, D. McLeod, J. Mol. Spectrosc. 17 (1965) 276.
- [17] A.N. Samoilova, Y.M. Efremov, L.V. Gurvich, J. Mol. Spectrosc. 86 (1981) 1–15.
- [18] C.F. Nelin, C.W. Bauschlicher, Chem. Phys. Lett. 118 (1985) 221.
- [19] L. Young, C.B. Moore, J. Chem. Phys. 81 (1984) 3137.
- [20] A. Leger, J.L. Puget, Astron. Astrophys. 137 (1984) L5.
- [21] L.J. Allamandola, A.G. Tielens, J.R. Barker, Astrophys. J. 290 (1985) L25.