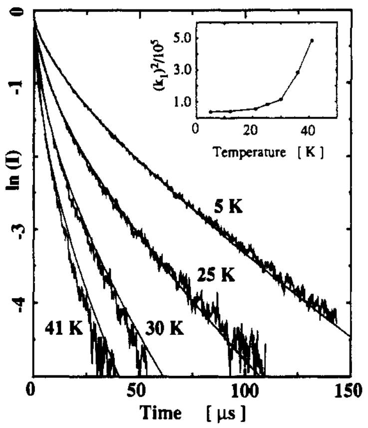

Figure 3. Normalized logarithmic plot of the emission decay curves of Pd^{II}(phbpy)Cl measured at 20 000 cm^{-1} for several temperatures. The full lines correspond to fits of the decay curves by eq 1 with $k_e = 14050$ s^{-1}. The insert shows the temperature dependence of the square of k_1.

compound supplied by Fluka had a nominal Pt impurity level of 120 ppm. From an X-ray fluorescence analysis of our samples we conclude that the synthesis and crystallization of Pd^{II}(phbpy)Cl leads to an accumulation of Pt(II) up to an order of magnitude of 0.1%.

In Figure 3 the decay curves of the intrinsic luminescence measured at 20 000 cm^{-1} are illustrated for four temperatures. We notice a considerable increase of the decay rate between 5 and 41 K, and we attribute this to nonradiative excitation energy migration through the Pd^{II}(phbpy)Cl lattice to the traps. The decay curves are nonsingle exponentials down to 5 K. This can have several reasons, and in the present system it is most likely due to a pronounced anisotropy of the energy migration. We have one of the very rare examples of a system in which the transfer rate in one dimension significantly exceeds the rates in the other directions, thus leading to a "slowing down" in the course of the luminescence decay process. The archetype 1-D transition-metal compound is tetramethylammonium manganese(II) chloride (TMMC), in which the luminescence decay curves show a very similar behavior and to which various theoretical models of exciton migration have been applied.[8,9] The decay curves in Figure 3 can reasonably be fitted by the function[10]

$$I = I_0 \exp(-k_e t - k_1 t^{1/2}) \qquad (1)$$

This function has been derived for 1-D energy migration in a lattice with an ordered distribution of impurities.[10] This assumption is likely to be incorrect in our case, but it has been shown that experimental data usually do not significantly discriminate between this equation (eq 1) and treatments that assume random distributions of the impurity.[8,9] In eq 1 k_1 is the rate constant for exciton trapping along the chain and k_e is the sum of the intrinsic decay rate k_i and a rate constant k_3, which takes into account three-dimensional energy migration to traps ($k_e = k_i + k_3$). The curves were fitted by a least-squares procedure before taking the logarithm of the intensity. For the 5 K curve both parameters k_e and k_1 were optimized whereas for all the other curves k_e was kept at its 5 K value. The 5 K values of k_e and k_1 are 14050 s^{-1} and 193 $s^{-1/2}$, respectively. The insert in Figure 3 shows the temperature dependence of the square of k_1, which is directly proportional to the 1-D hopping rate ν_1 as given by eq 2, where X_{trap} corresponds to the mole fraction of trap sites to

$$\nu_1 = \pi (k_1)^2 / [8(X_{trap})^2] \qquad (2)$$

Pd(II) sites.[10] With a trap concentration of around 0.1% we thus get a 1-D hopping rate of approximately 10^{11} s^{-1} at 41 K. This rate is about 10 times slower than the on-chain hopping rate in tetramethylammonium manganese(II) chloride at room temperature.[8,9] Recalling the one-dimensional stacked structure of the present compound, with a Pd–Pd separation of about 5.06 Å,[11] we find that the deduced order of magnitude of the transfer rate seems reasonable. The obtained 1-D hopping rate represents an upper limit, since k_e was kept at its 5 K value for fitting the curves at higher temperatures. Fits in which k_e was floated as well were not significantly better. For a more rigorous analysis of the decay curves a measurement of the intrinsic decay rate k_i in a dilute medium would be necessary. However, we have failed to find a suitable glass. All the glasses examined showed very large red shifts of the spectra, indicating that some changes occur in the first coordination sphere.

Nevertheless, we can get a lower limit of the one- to three-dimensional hopping rate ratio on the basis of the present results. The three-dimensional hopping rate, ν_3, can be approximated by[8]

$$\nu_3 \approx -\nu_1/2 + (\nu_1^2/4 + 0.8 k_3^2 / X_{trap}^2)^{1/2} \qquad (3)$$

Taking into account that $k_3 \le k_e$, we obtain an upper limit for ν_3 of 1×10^4 s^{-1} and a lower limit for the $\nu_1 : \nu_3$ ratio of 1×10^6 *at 5 K*. A pronounced one-dimensionality of the energy migration is therefore established.

Acknowledgment. We thank Professor R. Giovanoli for performing the X-ray fluorescence analysis of our samples.

Institut für Anorganische, Analytische und
Physikalische Chemie
Universität Bern
Freiestrasse 3
3000 Bern 9, Switzerland

Thomas Karlen
Andreas Ludi
Hans U. Güdel

Research School of Chemistry
The Australian National University
GPO Box 4
Canberra, ACT 2601, Australia

Hans Riesen*

Received July 31, 1990

---

(8) Auerbach, R. A.; McPherson, G. L. *Phys. Rev. B* **1986**, *33*, 6815.
(9) Knochenmuss, R.; Güdel, H. U. *J. Chem. Phys.* **1987**, *86*, 1104.
(10) Wieting, R. D.; Fayer, M. D.; Dlott, D. D. *J. Chem. Phys.* **1978**, *69*, 1996.
(11) Constable E.; Tocher, D. Private communication.

Bond Angle of CaF_2 in Several Host Matrices

In 1989, we published a note[1] indicating that infrared measurements of central metal atom isotope shifts for TiF_2 isolated in an argon matrix, which had been used to calculate an FTiF bond angle of ca. 120°, were in error. In addition, we questioned "how many of the results on high temperature molecules lead to *unambiguous* determination of the shape of the free molecule". Since that paper, we have shown[2] that, in a nitrogen matrix, $NiCl_2$ has a bond angle of ca. 130° using infrared isotope shift data and the harmonic approximation. This is in contrast to an argon matrix[2] where "The isotopic shift method ... cannot reliably detect any non-linearity". It is also known that the shapes of $ThCl_4$,[3] $CsUF_6$,[4] $CsNbF_6$,[5] and some pentachlorides[6] are martrix dependent.

For the group IIa dihalides, the heavier metals in combination with the more electronegative halogens appear to give the more strongly bent structures. The experimental techniques that have

---

(1) Beattie, I. R.; Jones, P. J.; Young, N. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 313.
(2) Beattie, I. R.; Jones, P. J.; Young, N. A. *Mol. Phys.*, in press.
(3) Beattie, I. R.; Jones, P. J.; Millington, K. R.; Willson, A. D. *J. Chem. Soc., Dalton Trans.* **1988**, 2759.
(4) Arthers, A.; Beattie, I. R.; Jones, P. J. *J. Chem. Soc., Dalton Trans.* **1984**, 711.
(5) Beattie, I. R.; Millington, K. R. *J. Chem. Soc., Dalton Trans.* **1987**, 1521.
(6) Ogden, J. S.; Levason, W.; Hope, E. G.; Graham, J. T.; Jenkins, D. M.; Angell, R. M. *J. Mol. Struct.* **1990**, *222*, 109.

0020-1669/91/1330-2250$02.50/0

Table I. Observations[a] of ν_3 of CaF_2 in Various Matrix Gases and Calculated Bond Angles

matrix	ν_3/cm^{-1}		
	^{40}Ca	^{44}Ca	θ/deg
neon	583.2_5	570.9_1	143
argon	559.5_2	547.6_5	144
	559.3_5[b]	547.5_6[b]	142
krypton	553.5_2	541.9_7	139
nitrogen	529.7_0	518.1_2	156
	529.5_8[b]	517.9_9[b]	156
carbon monoxide	494.3_1	483.5_1	155
argon–1% CO[c]	554.2_7	542.5_9	142

[a] Infrared spectrometer: Perkin-Elmer 983G (cold tip of Displex DE 204SL instrument at ca. 8 K). [b] Repeat set of experiments. [c] In the argon CO matrix, the "free" CaF_2 bands occur at 558.9_4 and 547.2_5 cm^{-1}, giving an angle of 139°.

been used to examine the structures of these molecules include the following: (1) electric deflection,[7] where the precise interpretation of the results is open to question; (2) electron diffraction,[8] where interatomic distances are averaged over all thermal vibrations and all species present in the vapor; (3) infrared spectroscopy of matrix isolated species using isotope shift data and/or the relative intensities of ν_3 and ν_1.[9,10] (The isotope shift method becomes less sensitive as the mass of the central atom increases, while the identification of ν_1 from infrared spectroscopy is by no means easy.)

Of the reputedly nonlinear group IIa dihalides, CaF_2 has two available isotopes, differing by four mass units (in ca. forty), and a relatively high antisymmetric stretching frequency (ν_3). Although rotationally resolved laser induced fluorescence spectra of some first-row transition-element dihalides have been obtained in a jet-cooled molecular beam,[11] the experimental difficulties in obtaining similar data for CaF_2 are formidable. We have therefore carried out infrared spectroscopic studies of CaF_2 using a range of matrix gases. In these experiments the CaF_2, which was prepared from $CaCO_3$ and aqueous hydrofluoric acid, was enriched by ^{44}Ca (Bureau des Isotopes Stable, Gif-sur-Yvette, France) to give a ^{40}Ca:^{44}Ca ratio of the order of 2:1. The matrix isolation technique used here has been described in detail elsewhere.[12]

We carried out preliminary measurements on natural-abundance CaF_2 in neon as this matrix is least likely to show strong guest–host interactions. Over the range 1000–200 cm^{-1} only one intense band was observed at 583.2_5 cm^{-1}, a shift of some 30 cm^{-1} to high frequency of the earlier ν_3 result in krypton found by Calder et al.,[10] who in addition reported ν_1 at 484.7_5 cm^{-1}. On this basis, ν_1 of CaF_2 in neon would be expected to occur in the region of 510 cm^{-1}. In several of our spectra, there was a weak band at 512 cm^{-1}, but it was of variable intensity relative to ν_3. In view of earlier difficulties in the identification of ν_1 of MgF_2,[13] the research reported here centers on isotopic shifts of ν_3 of CaF_2, with Figure 1 showing the infrared spectrum of $^{40,44}CaF_2$ isolated in a neon matrix in this region. The results of our investigations in neon, argon, krypton, nitrogen, and carbon monoxide are summarized in Table I. For the inert gases, the bond angle calculated for CaF_2 is ca. 141°. This result relies on the use of the harmonic approximation and does not allow for any apparent change in masses due to interaction with the host matrix. Our results in krypton agree with those of Calder et al.,[10] who gave an average bond angle of 140°.

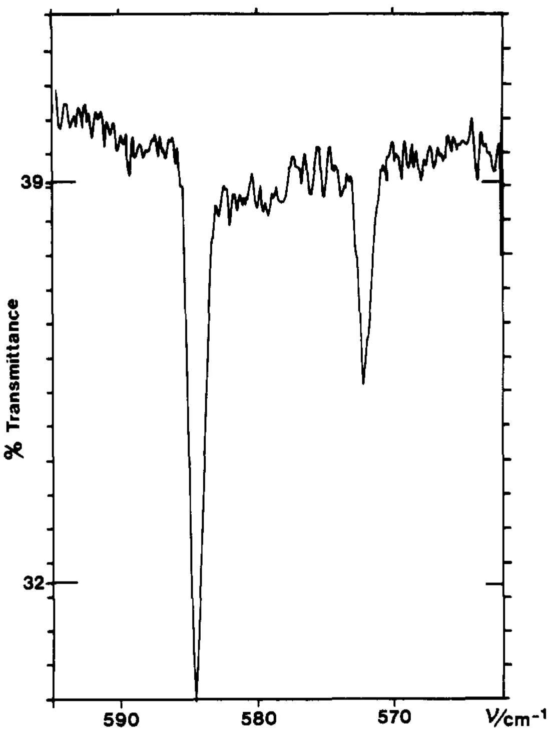

Figure 1. Infrared spectrum in the region of ν_3 for enriched CaF_2 (^{40}Ca:^{44}Ca ≈ 2:1).

For N_2 and CO matrices, the apparent bond angle is ca. 155°, with very large matrix shifts of about 50 and 90 cm^{-1}, respectively. It is interesting that, in an argon matrix doped with 1% CO, the band attributed by other workers[14] to the antisymmetric stretching mode of the 1:1 "adduct" CaF_2·CO yields a bond angle of 142° for the CaF_2 residue.

Our experimental results may be compared with calculations published this year (1990) giving bond angles of 130,[15] 152,[16] 155,[17] and 163°.[18] Salzner and Schleyer[19] comment that "Ab initio calculations with basis sets approaching the HF limit do not converge towards a certain bond angle". The paper by DeKock et al.[15] gives an excellent overview of this field. There is also an unpublished study[20] of CaF_2·CO giving a bond angle of 165°.

Acknowledgment. We thank Professor H. F. Schaefer for sending us a copy of a manuscript prior to publication, Professor J. M. Dyke and Dr. C. J. Marsden for helpful discussion, and the Science and Engineering Research Council of Great Britain for financial support.

Chemistry Department
Southampton University
Southampton SO9 5NH, U.K.

Ian R. Beattie*
Peter J. Jones
Nigel A. Young

Received October 26, 1990

---

(7) See for example: Wharton, L.; Berg, R. A.; Klemperer, W. *J. Chem. Phys.* **1963**, *39*, 2023. Buchler, A.; Stauffer, J. L.; Klemperer, W.; Wharton, L. *J. Chem. Phys.* **1964**, *40*, 3471. Buchler, A.; Stauffer, J. L.; Klemperer, W. *J. Am. Chem. Soc.* **1964**, *86*, 4544.

(8) Akishin, P. A.; Spiridonov, V. P.; Sobolev, G. A. *Zh. Fiz. Khim.* **1957**, *31*, 648. Kasparov, V. V.; Ezhov, Yu. S.; Rambidi, N. G. *Zh. Strukt. Khim.* **1979**, *20*, 260. Spiridonov, V. P.; Gershikov, A. G.; Altman, A. B.; Romanov, G. V.; Ivanov, A. A. *Chem. Phys. Lett.* **1981**, *77*, 41. Vajda, E.; Hargittai, M.; Hargittai, I.; Tremmel, J.; Brunvoll, J. *Inorg. Chem.* **1987**, *26*, 1171. Kasparov, V. V.; Ezhov, Yu. S.; Rambidi, N. G. *Zh. Strukt. Khim.* **1979**, *20*, 341.

(9) Snelson, A. *J. Phys. Chem.* **1966**, *70*, 3208. Ramondo, F.; Rossi, V.; Bencivenni, L. *Mol. Phys.* **1988**, *64*, 513. Ramondo, F.; Bencivenni, L.; Nuriziante Cesaro, S.; Hilpert, K. *J. Mol. Struct.* **1989**, *192*, 83. There has also been a gas-phase study of ν_2: Baikov, V. I. *Opt. Spectrosc.* **1968**, *25*, 356.

(10) Calder, V.; Mann, D. E.; Seshadri, K. S.; Allavena, M.; White, D. *J. Chem. Phys.* **1969**, *51*, 2093.

(11) Zink, L. R.; Grieman, F. J.; Brown, J. M.; Gilson, T. R.; Beattie, I. R. Unpublished observations.

(12) Beattie, I. R.; Blayden, H. E.; Hall, S. M.; Jenny, S. N.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1976**, 666.

(13) Lesiecki, H. L.; Nibler, J. W. *J. Chem. Phys.* **1976**, *64*, 871.

(14) Van Leirsburg, D. A.; DeKock, C. W. *J. Phys. Chem.* **1974**, *78*, 134.

(15) DeKock, R. L.; Peterson, M. A.; Timmer, L. K.; Baerends, E. J.; Vernooijs, P. *Polyhedron* **1990**, *9*, 1919.

(16) Dyke, J. M.; Wright, T. *Chem. Phys. Lett.* **1990**, *169*, 138.

(17) von Szentpály, L.; Schwerdtfeger, P. *Chem. Phys. Lett.* **1990**, *170*, 555.

(18) Hassett, D. M.; Marsden, C. J. *J. Chem. Soc., Chem. Commun.* **1990**, 667.

(19) Salzner, V.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1990**, *172*, 461.

(20) DeKock, R. L.; Remington, R. B.; Schaefer, H. F. Unpublished work.