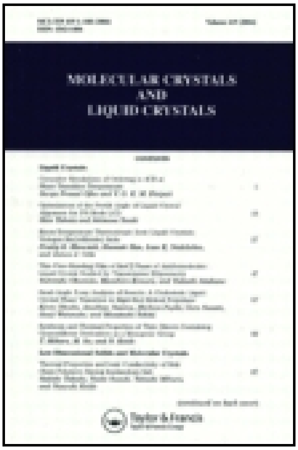

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Librational Excitations in Solid Acetylene and Carbon dioxide

Zeki Palabiyik [a]

[a] Teorik Fizik Kürsüsü, Fen Fakültesi, Istanbul and Institut fur Theoretische Physik, University of Giessen, Giessen

Version of record first published: 20 Apr 2011.

To cite this article: Zeki Palabiyik (1981): Librational Excitations in Solid Acetylene and Carbon dioxide, Molecular Crystals and Liquid Crystals, 65:1-2, 151-158

To link to this article: http://dx.doi.org/10.1080/00268948108076137

Mol. Cryst. Liq. Cryst., 1981, Vol. 65, pp. 151–158
0026-8941/81/6502-0151$06.50/0

Librational Excitations in Solid Acetylene and Carbon dioxide

ZEKI PALABIYIK

Teorik Fizik Kürsüsü, Fen Fakültesi, Istanbul and
Institut fur Theoretische Physik, University of Giessen, Giessen.

(*Received April 23, 1980: in final form May 5, 1980*)

The energies of the librational excitations of solid C_2H_2 and CO_2 are calculated in the RPA using intermolecular quadrupole forces only. While a classical theory of the librations seems to be sufficient for CO_2, in C_2H_2 a calculation between classical small angle librations and quantum crystal librons (like in solid hydrogen) is necessary. On the other hand it turns out that other forces apart from one electrostatic moment have to be taken into account to reproduce the measured data.

I INTRODUCTION

A number of substances of linear molecules crystalize at least in one phase in the Pa3 structure. The dynamics of such crystals have been considered most thoroughly in the case of *o*-hydrogen and *p*-deuterium. There the forces are relatively well known. Phonons and librons have been calculated including their coupling[1,2] and also including the anharmonicity of the librons.[3,4] But the solid hydrogens are typical quantum crystals not easily comparable with other solids.

In this paper we are interested in solid acetylene, C_2H_2 and carbondioxide, CO_2. We consider the dynamics for the librons alone and try to calculate their energies using only the quadrupole forces. Classical calculations of this kind have been performed by Walmsley and Pople[5] for CO_2 and by Ito *et al.*[6] for C_2H_2. In our calculation we determine the ground state in the Hartree approximation and get the librons via the RPA. Contrary to the case of hydrogen the moment of inertia of the molecules is much larger and the intermolecular forces are stronger. Therefore the molecules are relatively well localized and the librational ground state and the low lying excitations can be approximated with a Gaussian of the deviational angle. The width of the Gaussian is optimized by variation. Our calculation neglects the influence of temperature.

This paper has to be compared with the work of Jacobi and Schnepp.[8–10] These authors have emphasized the necessity of quantum mechanical lattice dynamics for the class of solids between the solid hydrogens and classical solids consisting of light molecules and weak forces. They propose a single particle approximation which is able to reproduce an acoustic behaviour of phonons (as the RPA does). As can be seen from the matrix elements which they use, their theory in general is equivalent to ours though more complicated. We compare approximations and results with ours in the discussion.

Since libronic energies are only known from Raman scattering, we need to know the three $\mathbf{k} = 0$ librons. The libron band width is given by the maximal difference of the $\mathbf{k} = 0$ energies.

In Section II we sketch the theory. The results are discussed in Section III.

II THE METHOD

We consider the rigid crystal with the Hamiltonian

$$H = \sum_{i=1}^{N} T_i + \frac{1}{2}\sum_{i\neq j} W_{ij} \qquad i, j = 1, 2, \ldots, N \tag{1}$$

where T_i is only the rotational kinetic energy and W_{ij} is the electrical quadrupol-quadrupol interaction. As one particle states we use

$$\phi^0 = \phi_{0,0} = B_0 \exp\left(-\frac{\omega_0 I}{2\hbar}\theta^2\right)$$

$$\phi^{\pm 1} = \phi_{1,\pm 1} = B_1 \theta \exp\left(-\frac{\omega_0 I}{2\hbar}\theta^2\right)\exp(\pm i\phi) \tag{2}$$

as ground state resp. excited states. θ and ϕ denote the orientation of the molecule relative to the body diagonal, associated with its simple cubic sublattice. I is the moment of inertia, ω_0 the oscillator frequency, which we vary to adjust for the optimal width of wave functions. We get this width from the Hartree ground state energy

$$E = \sum_{i=1}^{N} \langle \phi_i^0 | T_i | \phi_j^0 \rangle + \frac{1}{2} \sum_{i \neq j} \langle \phi_i^0 \phi_j^0 | W_{ij} | \phi_i^0 \phi_j^0 \rangle \tag{3}$$

The parameter ω_0 of minimal E is used in the following.

The RPA equations can be derived in one or the other of the well-known ways. We get

$$\begin{aligned} (\hbar\omega - \varepsilon^\alpha)\sigma_i^{\alpha 0} &= \sum_{j(\neq i)} \sum_{\beta} [\langle \alpha 0 | W_{ij} | 0\beta \rangle \sigma_j^{\beta 0} + \langle \alpha\beta | W_{ij} | 00 \rangle \sigma_j^{0\beta}] \\ -(\hbar\omega + \varepsilon^\alpha)\sigma_i^{0\alpha} &= \sum_{j(\neq i)} \sum_{\beta} [\langle 00 | W_{ij} | \alpha\beta \rangle \sigma_j^{\beta 0} + \langle 0\beta | W_{ij} | \alpha 0 \rangle \sigma_j^{0\beta}] \end{aligned} \tag{4}$$

for the amplitude $\sigma_i^{\alpha 0}$ resp. $\sigma_i^{0\alpha}$ of the excitation (see e.g.)[1] We have introduced the following abbreviations: $\varepsilon^\alpha = E^\alpha - E^0$, the single particle excitation energy in the Hartree approximation,

$$\langle \alpha\beta | W_{ij} | \gamma\delta \rangle = \langle \phi_i^\alpha \phi_j^\beta | W_{ij} | \phi_i^\gamma \phi_j^\delta \rangle$$

where $\alpha, \beta, \gamma, \delta = 0, \pm 1$. The RPA Eq. (4) can be solved with the ansatz

$$\sigma_i^{\alpha 0} + \sigma_i^{0\bar{\alpha}} = \sigma_{\mathbf{m},g}^{\alpha 0} + \sigma_{\mathbf{m},g}^{0\bar{\alpha}} = C_g^\alpha e^{i\mathbf{k}\cdot\mathbf{R}_i}$$

with $\mathbf{R}_i = a(\mathbf{m} + \mathbf{r}_g)$. The lattice site i is more exactly characterized by its cell index $\mathbf{m}$ and the sublattice index g $(=0, 1, 2, 3)$. We are led to the secular equation

$$\hbar\omega_B C_g^\alpha = \sum_{\beta, h} \left[\varepsilon\delta_{gh}^{\alpha\beta} + \sum_{\mathbf{n}} e^{i\mathbf{k}\cdot\mathbf{R}_{ij}} \langle \phi_g^\alpha \phi_h^0 | W_{ij} | \phi_g^0 \phi_h^\beta \rangle \right] C_h^\beta$$

with

$$j = (\mathbf{n}, h), \mathbf{R}_{ij} = \mathbf{R}_j - \mathbf{R}_i, \varepsilon = \varepsilon^\alpha = \varepsilon^{\bar{\alpha}}$$

and

$$\hbar\omega_B = \frac{\hbar^2\omega^2 + \varepsilon^2}{2\varepsilon}$$

This equation is solved for nearest neighbour interactions only. The Pa3 symmetry allows one to reduce the number of matrix elements to only two, e.g.

$$\langle \phi_0^1 \phi_1^0 | W_{01} | \phi_0^0 \phi_1^1 \rangle = \lambda \frac{50\pi^3}{27} I_1^2 (1 - 5\sqrt{3}i)$$

$$\langle \phi_0^1 \phi_1^0 | W_{01} | \phi_0^0 \phi_1^{-1} \rangle = -\lambda \frac{10\pi^3}{27} I_1^2 (37 + 25\sqrt{3}i)$$

where

$$I_1 = \int_0^{\infty} \phi^0(\theta) Y_{2,1}(\theta) \phi^{+1}(\theta) \sin\theta \, d\theta$$

with $Y_{2,1}(\theta)$ the spherical surface function without the factor $e^{i\phi}$. The integral can be expressed by Kummer-functions.

The solution of the secular equation for $\mathbf{k} = 0$ is analogous to Mertens[1] and results in the following three libron frequencies:

$$\omega_1^{RPA} = \frac{\varepsilon}{\hbar}\left[1 + \lambda \frac{160\pi^3}{3\varepsilon} I_1^2 (R + 2|A|)\right]^{1/2}$$

$$\omega_2^{RPA} = \frac{\varepsilon}{\hbar}\left[1 + \lambda \frac{160\pi^3}{3\varepsilon} I_1^2 (R - 2|A|)\right]^{1/2}$$

$$\omega_3^{RPA} = \frac{\varepsilon}{\hbar}\left[1 - \lambda \frac{160\pi^3}{\varepsilon} I_1^2 R\right]^{1/2}$$

with the abbreviations

$$R = \frac{20}{9}, A = \frac{37 + 25\sqrt{3}i}{18}$$

$$\lambda = \frac{6}{25} \frac{q^2}{R_0^5}$$

(q permanent quadrupol moment, R_0 nearest neighbour distance).

Here ω_1 and ω_2 are triplets, ω_3 a doublet.

III DISCUSSION OF THE RESULTS

We begin the discussion with our numerical results and compare them with other calculations and with experiment.

a) Acetylene The variation of the ground state energy leads to the width parameter $\omega_0 I/\hbar = 24.7$. With this parameter we get the *RPA* frequencies of Table I. We have used the following numerical values:

$$q = 3 \cdot 10^{-26} \text{ esu, C—C} = 1.20 \text{ Å, C—H} = 1.05 \text{ Å, } a_0 = R_0\sqrt{2} = 6.14 \text{ Å.}$$

The *RPA* frequencies are smaller and therefore nearer to the experiment than Ito's but not small enough. Ito has used the classical libron theory of Walmsley and Pople. The variational and *RPA* treatment results in a certain improvement but it is not large enough. Our calculation neglects

TABLE I

Libron frequencies for C_2H_2 in the high-temperature phase in cm^{-1}

Experiment of Ito *et al.*[6] 173°K	Calculated by Ito *et al.*[6]	This work RPA
22	34	32
33	48	45
67	87	82

the temperature and is somewhat inadequate to the Pa3 phase of C_2H_2 which is stable only above 133°K. The difference to the measured frequencies can be traced back in part to our neglection of the temperature. But another part can only be removed by lifting our simplifying assumption of a rigid lattice and by introducing dispersion forces.

b) Carbondioxide Here $\omega_0 I/\hbar = 76.4 \, q = -4.1 \cdot 10^{-26}$ esu, $a_0 = R_0\sqrt{2} = 5.574$ Å, C—O = 1.13 Å. Table II contains the measurements and the calculations.

TABLE II

Libron frequencies for CO_2 in cm^{-1}

Experiment Gaizauskas 213°K	Experiment Cahill *et al.* 100°K	Calculated by Walmsley and Pople	This work RPA
64	73	35	34
77	90.5	48	48
112	131	88	88

The difference of the calculations is negligible. This reflects the fact that the CO_2 is already a very classical crystal. The difference between theory and experiment is larger yet than for C_2H_2. The molecule of CO_2 has such extended electron clouds compared to the lattice constant that it is not a good approximation at all to neglect the dispersion forces and to imitate the electrostatic forces with only one moment, the quadrupol moment q.

Our paper was stimulated by the success of the theory of hydrogen crystals. Since C_2H_2 seems to be in between typically classical crystals like CO_2 and typically quantum crystals like solid hydrogen, we were interested to find out how far the modified hydrogen theory would reach. In the end we can conclude: Quantum correction are relatively small already for C_2H_2, they can be neglected for CO_2. Dispersion forces seem to be of larger influence, refined electrostatic forces too.

In comparison of Jacobi and Schnepp's results with ours we firstly consider the starting point: The one-particle structure of the states is the same, also the variational parameter. We have neglected the Pauli principle since we wanted not to consider the (small) influence of the nuclear spin on the dynamics. We have also restricted our calculations to nearest neighbours only. Comparison is possible only for the case of CO_2. The resultant Raman frequencies are more different than we expected them to be (see Table III). Our values are nearer to the classical ones though both are far from the experimental frequencies. We don't know, where the differences in the calculations come from.

TABLE III

Calculated librational frequencies for CO_2 in cm^{-1}. The molecular quadrupol moment used in the calculations is 4.3×10^{-26} esu. cm^2.

	Nearest neighbours only		
	Classical	Quantum[a]	RPA
E_g	36.2	42.5	38
T_g	50.0	51.3	50
T_g	91.5	94.8	91

[a] Reference.[10]

In the future, calculations using only quadrupole forces can lead only to estimates. But it is clear in what direction better calculation can be performed: Better forces are already available for C_2H_2 from the work of Kihara and coworkers.[7] (To this question see also the work of Suzuki and Schnepp).[11]

They are more complicated to handle and it would be necessary to include phonons in the theory. Such a more involved calculation would also include temperature dependences. It would be worthwhile to do so in the near future because so easily measurable data as the Raman libron (and phonon) frequencies show fundamental properties of the dynamics of relatively simple molecular crystals. The refined theory sketched above could show whether our ideas about the intermolecular forces are correct or not.

Acknowledgment

The author would like to express his deep appreciation for help, stimulation and criticism to Professor W. Biem.

References

1. F. G. Mertens, W. Biem, and H. Hahn, *Z. Physik*, **213**, 33 (1968); F. G. Mertens, W. Biem, and H. Hahn, *Z. Physik*, **220**, 1 (1969); and other literature cited there.
2. F. G. Mertens, *Z. Physik*, **250**, 1 (1972); F. G. Mertens and W. Biem, *Z. Physik*, **250**, 273 (1972); and other literature cited there.
3. A. B. Harris and C. F. Coll III, *Phys. Rev.*, **134**, 2781 (1971).
4. A. B. Harris and A. J. Berlinsky, *Phys. Rev.*, **B7**, 4720 (1973).
5. S. H. Walmsley and J. A. Pople, *Mol. Phys.*, **8**, 345 (1964).
6. M. Ito, T. Yokoyama, and M. Suzuki, *Spectrochim. Acta*, **26A**, 695 (1970).
7. K. Sakai, A. Koide, and T. Kihara, *Chem. Phys. Letters*, Vol. 47, **3**, 416 (1977).
8. O. Schnepp and N. Jacobi, *Advan. Chem. Phys.*, **22**, 205 (1972).
9. N. Jacobi, *J. Chem. Phys.*, **57**, 6, 2505 (1972).
10. N. Jacobi and O. Schnepp, *J. Chem. Phys.*, **57**, 6, 2516 (1972).
11. M. Suzuki and O. Schnepp, *J. Chem. Phys.*, **55**, 11, 5349 (1971).