

of the structure occurring because of some voids in the lattice (e.g. vacancies) is possible starting from T_{th} . However, the temperature should always be raised to T_g to induce any significant change of the structure. Two such temperature barriers occurring in the transformation $2H-4H$ were reported by Minagawa (1978).

This work was sponsored by the Institute of Physics of the Polish Academy of Sciences.

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The Effect of Internal Vibration upon Deformation Densities and X-ray Scattering Intensities in H₂O and CO₂

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(Received 30 April 1985; accepted 3 March 1986)

Abstract

The vibrational averages of electron deformation densities and molecular X-ray scattering intensities have been calculated for the bend vibration in H₂O and CO₂, and for the symmetric stretch vibration in H₂O. It is shown that bend mode vibrations, despite their relatively large amplitudes, have a minor effect on deformation densities and X-ray scattering intensities. Together with previous results for stretch vibration in diatomic molecules, which have been confirmed by the results in this paper for stretch vibration in triatomics, this means that all internal vibrations may be neglected except for the smearing of the high peaks very close to the nuclei. Since the X-ray intensities associated with this area will be found at high S values, the effect upon scattering intensities at low S is not important. In the valence region the effects are negligible compared to other sources of error in the comparison of calculations with experiment, such as basis set, libration [cf. Hermansson (1983). *Chem. Phys. Lett.* **99**, 295-300] etc.

I. Introduction

The effect of vibrational averaging on calculated observables has been studied mostly for the stretch vibration in diatomic molecules. Among others, detailed studies have been reported for effects in both reciprocal (scattering) space (Stewart, 1977; Epstein & Stewart, 1979) and position space (Rozendaal & Ros, 1982; and references therein). The stretch vibration proved to be of minor importance, yielding only small corrections to, for example, the static deformation density at R_e due to the small weight of other internuclear distances in the vibrational average. It is possible that the influence of bend vibrations is larger, as the force constants are in general smaller and the vibration amplitudes larger. We will therefore study in this paper the internal vibration modes of the triatomic molecules H₂O and CO₂, employing the same method as used before in our study on diatomic molecules. It is interesting to consider the vibrational motion of hydrogens as the root-mean-square (r.m.s.) displacements are relatively large. Hydrogens on the

other hand carry little electron density, so it seemed worthwhile to include the motion of heavier atoms, as in CO₂. The influence of vibrational averaging on both the electron deformation densities and the X-ray scattering intensities will be considered. The information obtained in reciprocal space has the well known Fourier transform property: it will show at low momentum in particular the effect upon the diffuse part of the electron density in position space (Coppens, 1982).

II. Method

The larger number of degrees of freedom for the nuclear motions makes a study of vibrational effects in a triatomic system more complicated than in a diatomic one. In order to obtain an impression of the influence of individual modes within a simplified description, we start with the calculation of the effect for pure stretch and pure bend vibrations. In this way we can, without undue complications, describe the nuclear motion by a one-dimensional vibrational wavefunction for each mode, *i.e.* we use just one internal symmetry coordinate [either $S_1 = (1/\sqrt{2}) \times (\delta r_1 + \delta r_2)$ or $S_2 = \delta \theta$] to describe the nuclear motion. In this way it is possible to incorporate the anharmonicity of the nuclear motion in the one-dimensional wavefunctions. As the anharmonicity is important for the possible effect of vibrational averaging we feel this procedure to be more adequate than the use of a harmonic normal mode of vibration. It would also be possible to calculate an anharmonic vibrational wavefunction in a normal coordinate Q , but in view of the large amplitude for the bending mode, for example, this would imply large linear displacements of the nuclei which are probably less realistic than the motion according to the pure curvilinear symmetry coordinate (Hoy, Mills & Strey, 1972). The relevance of these approximate calculations of the smearing effect for the actual (anharmonic, non-normal) vibration will be considered afterwards.

The method used for these computations is analogous to the method used for the averaging of the deformation density in diatomics due to the internal vibration. A detailed description of the method has been given before (Rozendaal & Ros, 1982), so here we restrict ourselves to a brief account. Assuming that the electronic system will be described correctly by its adiabatic ground-state wavefunction, with electron density $\rho(\mathbf{r}; \mathbf{R})$, the time average of this density can be found from

$$\rho_{\text{int}}(\mathbf{r}) = \sum_n W_n \int \psi_n^*(\mathbf{R}) \rho(\mathbf{r}; \mathbf{R}) \psi_n(\mathbf{R}) d\mathbf{R}, \quad (1)$$

where $\psi_n(\mathbf{R})$ is the nuclear wavefunction for vibrational state n with W_n the Boltzmann weight factor belonging to this state. In a previous study we have shown that for these model calculations equation (1)

may be simplified by supposing that vibrational smearing can be described with an acceptable degree of accuracy by taking into account only the ground-state vibrational wavefunction,

$$\rho_{\text{int}}(\mathbf{r}) = \int \psi_0^*(\mathbf{R}) \rho(\mathbf{r}; \mathbf{R}) \psi_0(\mathbf{R}) d\mathbf{R}. \quad (2)$$

This simplification can also be made in the present study as the frequency of the bend mode (the lowest frequency mode for the two triatomic molecules) of CO₂ is 675 cm⁻¹, corresponding to an Einstein temperature of 950 K. Thermal population of excited vibrations is thus irrelevant to this study.

Furthermore, as only one of the symmetry coordinates (R_1) will be varied (the others remaining constant) we have

$$\rho_{\text{int}}(\mathbf{r}; R_2 \dots R_n) = \int \psi_0^*(R_1) \rho(\mathbf{r}; \mathbf{R}) \psi_0(R_1) dR_1. \quad (3)$$

The vibrational wavefunction is expanded in harmonic oscillator eigenfunctions $\varphi_i(R)$,

$$\psi_0(R) = \sum_{i=0}^m a_i \varphi_i(R), \quad (4)$$

with

$$\varphi_i(R) = N_i H_i(R\sqrt{\alpha}) \exp(-\alpha R^2/2), \quad (5)$$

H_i being a Hermite polynomial and N_i the normalization constant.

The integration over R_1 in (3) is carried out numerically using the Gauss-Hermite integration technique (Abramowitz & Stegun, 1964). The final expression to be evaluated is

$$\rho_{\text{int}}(\mathbf{r}; R_2 \dots R_n) = \frac{1}{\sqrt{\alpha}} \sum_{i=0}^n \rho\left(\mathbf{r}; \frac{X_i}{\sqrt{\alpha}}, R_2 \dots R_n\right) Q(X_i) W_i, \quad (6)$$

with X_i the zero points of the n th-order Hermite polynomial, W_i the integration weight factors and

$$Q(X_i) = \left[\sum_{j=0}^m a_j N_j H_j(X_i) \right]^2. \quad (7)$$

The effect of internal vibration upon molecular X-ray scattering intensities has been calculated in an analogous way. The X-ray form factor corresponding to a particular value of \mathbf{R} can be written (Epstein & Stewart, 1979, 1980)

$$F(\mathbf{S}; \mathbf{R}) = \int \rho(\mathbf{r}; \mathbf{R}) \exp(i\mathbf{S} \cdot \mathbf{r}) d\mathbf{r}, \quad (8)$$

and the elastic X-ray scattering intensity

$$I(\mathbf{S}; \mathbf{R}) = F^*(\mathbf{S}; \mathbf{R}) F(\mathbf{S}; \mathbf{R}). \quad (9)$$

Restricted again to the electronic and vibrational ground-state wavefunctions, the vibrational average of the X-ray intensity for internal coordinate R_1

becomes:

$$I_{\text{int}}(\mathbf{S}; R_2 \dots R_n) = \int \psi_0^*(R_1) I(\mathbf{S}; \mathbf{R}) \psi_0(R_1) dR_1 \quad (10)$$

$$\approx \frac{1}{\sqrt{\alpha}} \sum_{i=0}^n \rho\left(\mathbf{S}; \frac{X_i}{\sqrt{\alpha}}, R_2 \dots R_n\right) Q(X_i) W_i.$$

The molecular form factors have not been computed directly from the electronic wavefunctions. Instead, the total charge density was expanded into sets of spherical harmonic functions multiplied by a Slater-type radial function, centered at each nucleus,

$$\rho(\mathbf{r}; \mathbf{R}) \approx \sum_i c_i f_i(\mathbf{r}; \mathbf{R}). \quad (11)$$

The coefficients c_i were computed by an analytical least-squares fit of the charge density, constrained to the total number of electrons (Baerends & Ros, 1978). It should be noted that the charge density was not divided into a number of atomic fragments, but a separate fit of the molecular density was made for each nuclear configuration. The full orbital (and density) relaxation is thus included in the present scheme. The Fourier transformation of the position space density represented by single-centre functions [equation (11)] could be performed analytically (Kajiser & Smith, 1977). The form factors were normalized to the number of electrons at $S = 0$.

III. Results and discussion

Model calculations have been performed for the bend mode in H₂O and CO₂, and for the symmetric stretch in H₂O. The effect of the CO₂ stretch mode is expected to be comparable to the CO stretch vibration, which has been considered before. For the internal displacement R of the bend mode we have chosen the curvilinear bend coordinate $\delta\theta$; the stretch coordinate was $(\delta r_1 + \delta r_2)/\sqrt{2}$. The values of α in the Hermite polynomial expansion were calculated from the experimental force constants and the frequencies of the predominantly bend or stretch vibration, using the relation $\alpha = k/\omega$ (in a.u.) (*cf.* Table 2). Note that these values are not critical in our calculation since a large number (30) of Hermite functions was included in the expansion of the vibrational wavefunctions. For all calculations we used Hartree-Fock-Slater LCAO-SCF electronic wavefunctions (Baerends & Ros, 1978). The basis sets were of triple- ζ quality, extended with two p -function sets for the hydrogen atom, and two d -function sets for the carbon and oxygen atoms. The nuclear displacements corresponding to the n integration points X_i [equation (6)] were chosen as the zeros of the 31st Hermite polynomial. Electronic wavefunctions were actually computed at only 21 nuclear displacements as the remaining ten displacements are associated with weight factors in equations (6) and (10) below

Table 1. *Experimental and theoretical geometries and force constants, calculated r.m.s. amplitudes of pure bend and pure stretch vibrations [for experimental values see Hoy et al. (1972), Smith & Overend (1971) and Mills (1974)]*

	H ₂ O		CO ₂	
	exp.	HFS	exp.	HFS
R (a.u.)*	1.8088	1.81	2.1921	2.197
f_{RR} (mdyn Å ⁻¹)†	8.353	7.94	17.28	16.95
RMS (a.u.)		0.14		
θ (°)	104.52	104.55	180.00	180.00
f_θ (mdyn Å)	0.697	0.70	0.785	0.65
RMS (°)		8.60		5.59
D_e (eV)‡	10.08	9.6	16.85	18.7

* 1 a.u. = 0.529177 × 10⁻¹⁰ m.
 † 1 mdyn = 10⁻⁸ N.
 ‡ 1 eV = 1.6 × 10⁻¹⁹ J.

Table 2. *Expansion coefficients of vibrational wavefunctions in Hermite polynomials (B: bend vibration in H₂O and CO₂; S: symmetric stretch vibration in H₂O)*

	HOH-B	OCO-B	HOH-S
α	21.289	58.731	30.741
a_0	0.99969	0.99923	0.98279
a_1	0.02117	0.	0.18013
a_2	-0.01258	0.03911	0.02921
a_3	-0.00160	0.	0.02677
a_4	-0.00232	-0.00214	0.00933
a_5	-0.00307	0.	0.00240
a_6	0.00133	-0.00002	0.00158
a_7	0.00077	0.	0.00067
a_8	-0.00037	0.00003	0.00024

1.0E-8, which are negligible. The nuclei were positioned in the yz plane, a twofold axis coinciding with the z axis.

In Table 1 are shown the experimental geometry and force constants of the molecules. The calculated equilibrium bond angle of H₂O (at the experimental O—H distance) does not differ significantly from the experimental angle. The harmonic force constants from our calculations are also displayed in Table 1. The value for H₂O is very close to the experimental value, that for CO₂ appears to be slightly too small. The r.m.s. amplitudes of the vibration are listed in Table 1. The most important expansion coefficients of the vibrational wavefunctions in Hermite polynomials are given in Table 2; the total number of terms in this expansion [*cf.* equation (4)] was 30. These wavefunctions were computed variationally following the same procedure as was used for the vibrational wavefunctions of diatomic molecules (Rozendaal & Ros, 1982). It can be seen from the coefficients that the symmetric stretch contains considerably more anharmonic character than the bend mode wavefunctions.

The effects of the internal vibrations upon the electron density in H₂O are shown by the density difference maps in Fig. 1. The subtracted atomic

densities are values from spin-restricted HFS-LCAO calculations in the same basis sets as used for the molecule, with equal vibrational smearing (*i.e.* the promolecule is assumed to vibrate in the same way as the actual molecule). In both stretch and bend modes the effect appears to be most important in the positive area around the hydrogen nuclei. We note that the peak at the H nucleus is smeared out in both cases: due to the bending motion the two highest contours disappear, due to stretching motion only the highest contour. As expected, the bending motion leads to a lateral smearing (*i.e.* broadening in the direction perpendicular to the OH bond), whereas the stretching motion has more effect along the OH axis. In the case of a bend vibration the effect is slightly stronger than for the stretch vibration, as expected from the difference in force constants and r.m.s. amplitudes. The differences between all of the deformation densities, including the static deformation density, are small, however. In Fig. 2 are plotted the static and bend-averaged deformation densities of CO₂ along the *z* axis, that is, the axis through the carbon atom perpendicular to the bond axis and in

the plane of motion (the carbon has the largest amplitude in the bend vibration in which the center of mass stays at the origin). The major effect in this case is the relatively large change in the negative part of the difference density close to the carbon nucleus. Again, the influence of the bend vibration upon the deformation density is small.

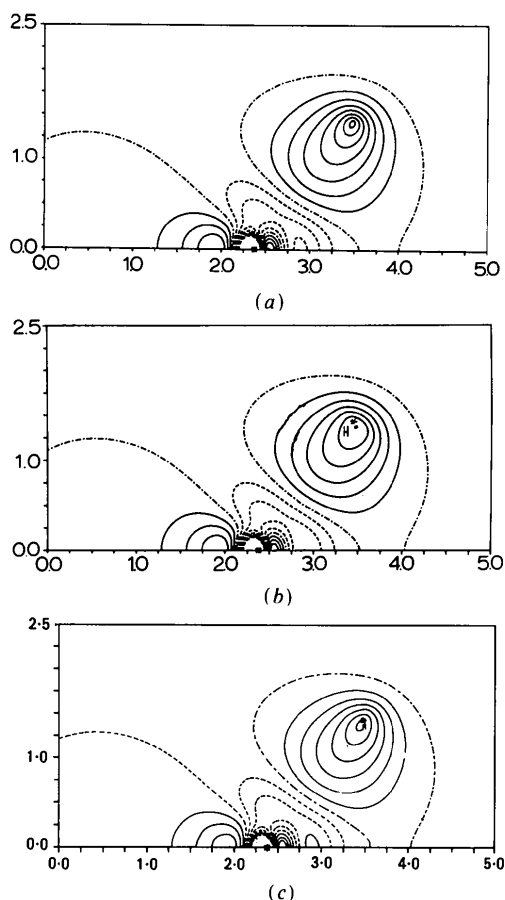


Fig. 1. Deformation density of H₂O in the plane of the molecule: (a) static, (b) average bend vibration, (c) average over symmetrical stretch vibration. Contours at 0.0, 0.03, 0.06, ..., 0.18, 0.21 e a.u.⁻³; solid lines: positive, dashed: negative, dash-dot: zero.

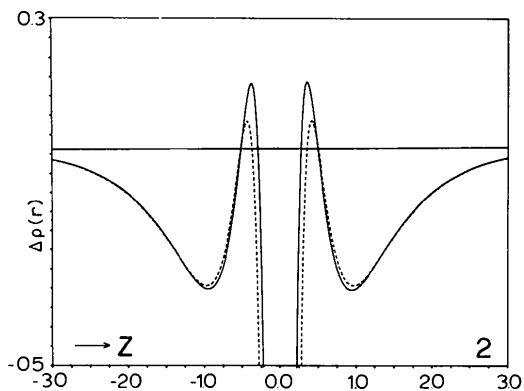


Fig. 2. Deformation density along the *z* axis in CO₂. Solid line: static; dashed line: average of bend vibration.

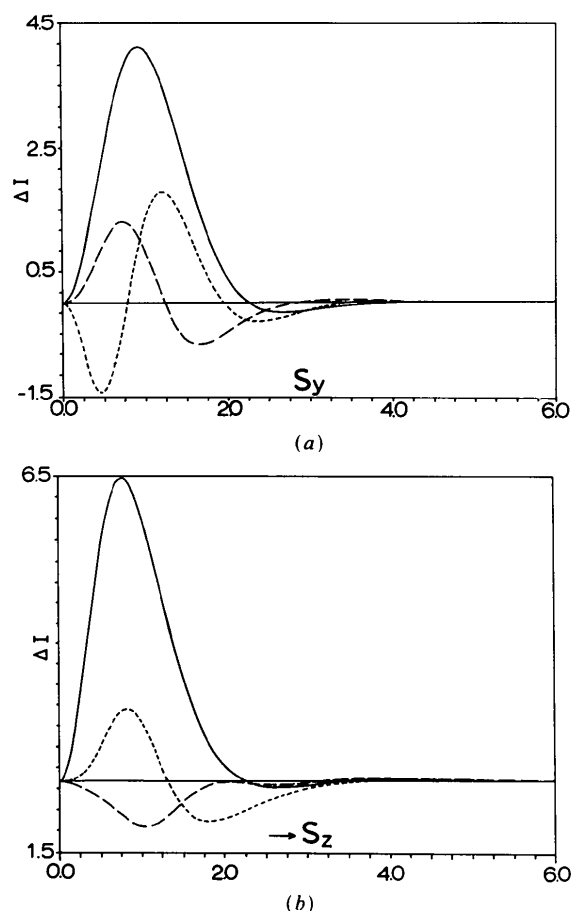


Fig. 3. Difference X-ray intensity ($\Delta I_{\text{sta}} = I_{\text{mol}} - I_{\text{promol}}$) of H₂O with scaled corrections [$I_{\text{cor}} = 10 \times (\Delta I_{\text{int}} - \Delta I_{\text{sta}})$] for vibrational smearing; short dash: bend correction; long dash: stretch correction; solid lines: static. (a) *S_y* axis. (b) *S_z* axis.

X-ray scattering intensities for both H₂O and CO₂ were computed in the x , y and z directions as functions of S_x , S_y and S_z . The CO₂ molecule lies along the y axis, and the H₂O molecule is in the yz plane, with the C_2 axis along the z axis; all vibrations are in the yz plane. The intensities in the S_x direction are practically not influenced by the vibrations in the yz plane. The results for the S_y and S_z directions are given in Figs. 3 and 4. $\Delta I_{\text{sta}} = I_{\text{mol}} - I_{\text{promol}}$ is the difference between the scattering intensity of the (static) molecular charge density and the intensity due to the promolecule, i.e. the superposition of the atomic charge densities with the atoms placed at their positions in the molecule:

$$\rho_{\text{promol}}(\mathbf{r}) = \sum_A \rho_A(\mathbf{r} - \mathbf{R}_A).$$

Defining the atomic form factors as

$$F_A(\mathbf{S}) = \int \rho_A(\mathbf{r}) \exp(i\mathbf{S} \cdot \mathbf{r}) d\mathbf{r}$$

and the atomic scattering intensity as $I_A = |F_A|^2$, it is clear that I_{promol} differs from $\sum_A I_A$:

$$\begin{aligned} F_{\text{promol}} &= \sum_A \exp(i\mathbf{S} \cdot \mathbf{R}_A) F_A \\ I_{\text{promol}} &= |F_{\text{promol}}|^2 \\ &= \sum_A I_A + \sum_{A \neq B} \exp[i\mathbf{S} \cdot (\mathbf{R}_A - \mathbf{R}_B)] F_A F_B^*. \end{aligned}$$

We are interested in the effect of bond formation, i.e. in the change with respect to I_{promol} rather than $\sum_A I_A$.

The effect of the internal vibrations is plotted as a scaled correction to ΔI_{sta} , $I_{\text{cor}} = 10 \times (\Delta I_{\text{int}} - \Delta I_{\text{sta}})$. From Figs. 3(a) and 3(b) it is clear that the absolute values of the correction for the bend vibration in water are slightly larger than those for the stretch vibration at low values of S_y and S_z , but the sign is opposite. The corrections can be viewed as small shifts of the main peak of ΔI . For the bend vibration this shift is to higher values of S_y and to lower S_z ; the effect of the stretch vibration is opposite. In Fig. 4 are plotted the corresponding curves for the bend mode in CO₂. The corrections are considerably smaller than those for H₂O. Note that the rather strong change in the position space deformation density near the carbon nucleus does not occur in the low- S -region intensities.

It is evident that the effect of the bend vibrations on both real-space deformation densities and X-ray scattering intensities is very minor indeed. We note that our results are based on pure stretch and pure (curvilinear) bend vibrations. In view of the very small effects found it is no use extending the calculations to more sophisticated vibrational wavefunctions.

Concerning the HFS method, we found that the calculated equilibrium geometry for H₂O is very good (cf. also Müller, Jones & Harris, 1983). This holds

for both the bond angle and the bond length. Computed force constants for both H₂O and CO₂ show reasonable accuracy as well.

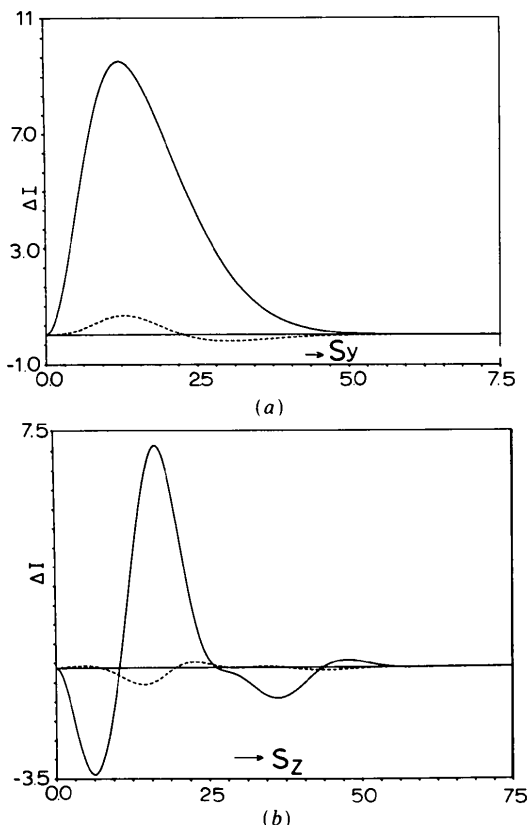


Fig. 4. Difference X-ray intensity of CO₂ with scaled corrections (see caption of Fig. 3) for averaging over bend vibrations. (a) S_y axis. (b) S_z axis.

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