Transition Dipole Interaction and Intermolecular Potential of Carbon Disulfide and Sulfur Dioxide Crystals

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The optical active normal frequencies and the heats of sublimation of carbon disulfide and sulfur dioxide crystals have been calculated. The interaction between the transition dipoles associated with the infrared active intermolecular modes has been taken into account by introducing coupling terms between the equivalent coordinates of neighboring molecules. The coupling force constants estimated from the infrared absorption intensities explain the observed trend of the factor group splittings of the ν_3 mode of carbon disulfide and the ν_1 and ν_3 modes of sulfur dioxide. The splitting of the ν_2 mode of carbon disulfide has been reproduced by taking account of the long range Coulomb interaction between the atomic charges.

Appreciable factor group splittings in infrared and Raman spectra of crystals often arise from the interaction between the transition dipoles associated with the vibrations of neighboring molecules or ions.[1,2] The most straightforward way of incorporating this interaction in the potential function of crystal lattices is to introduce appropriate coupling constants between the equivalent coordinates of adjacent molecules in a unit cell. As shown by Decius,[3] such a coupling constant can be evaluated from the derivative of the molecular dipole moment with respect to the internal or the normal coordinate concerned.

For the crystals of alkaline earth carbonates, the dipole moment derivatives estimated from the factor group splittings agree with those obtained from the infrared reflection spectra.[4] On the other hand, the intermolecular coupling constants for the crystals of hydrogen chloride[5] and methyl chloride[6] have not fully been explained by the dipole moment derivatives obtained from infrared band intensities. Further studies are thus required to establish the theoretical basis of the coupling constants introduced empirically.

In this work, we have aimed at evaluating the intermolecular potential functions of carbon disulfide and sulfur dioxide crystals, and at clarifying how far the effect of the coupling terms are manifested in the observed vibrational spectra. In order to check the validity of the adopted potential parameters, the values of the potential functions for the equilibrium structure have also been calculated and compared with the heat of sublimation.

Method of Calculation

The frequencies of the optical active inter- and intramolecular normal modes were calculated according to the method of Harada and Shimanouchi.[7] The quadratic intramolecular force constants are those of the general valence type fitted to the observed fundamental frequencies in the gaseous state.[8] They are given in Table 1. The atomic coordinates were taken from the X-ray studies by Baenziger and Duax for carbon disulfide[9] and by Post *et al.* for sulfur dioxide.[10]

In order to distinguish the role of various types of intermolecular interactions, calculations were made for three kinds of intermolecular potentials. In calculation I, we took into account only the short range interactions due to the exchange repulsion and the van der Waals attraction, using the potential in the exp-6 form

$$V_{\rm I} = \sum_{i,j} [-Ar_{ij}^{-6} + B\exp(-Cr_{ij})], \tag{1}$$

where r_{ij} is the distance between the atoms i and j. Table 2 shows the values of the parameters A, B and C for the C⋯C, S⋯S and O⋯O interactions adopted in the present work.[11,12] The parameters for the asymmetrical C⋯S and S⋯O interactions were estimated from those for the two corresponding symmetrical interactions by taking the geometric means for A and B and the arithmetic means for C.[13] The summation limit for this short-range interaction was taken to be 6 Å.

Calculation II was carried out for the potential including the coupling terms due to the transition dipole interaction in the form

$$V_{\rm II} = V_{\rm I} + \sum_{a,b} \sum_{i} K_i^{ab} S_i^a S_i^b, \tag{2}$$

where S_i^a and S_i^b denote the i-th internal symmetry coordinate of the molecules a and b, respectively, and K_i^{ab} is the coupling force constant related to these coordinates. The summation limit was taken to cover only the nearest-neighbor interaction. The coupling constant was calculated, according to Decius,[3] by

$$K_i^{ab} = |\partial\mu/\partial S_i|^2[(\boldsymbol{e}_a \times \boldsymbol{R})\cdot(\boldsymbol{e}_b \times \boldsymbol{R}) - 2(\boldsymbol{e}_a\cdot\boldsymbol{R})(\boldsymbol{e}_b\cdot\boldsymbol{R})]/|\boldsymbol{R}|^5, \tag{3}$$

where $\boldsymbol{e}_a$ and $\boldsymbol{e}_b$ are the unit vectors along the transition dipoles formed in the molecules a and b, respectively, and $\boldsymbol{R}$ is the vector joining these dipoles. The transition dipoles were assumed to be at the central atoms (C for carbon disulfide and S for sulfur dioxide) for all the infrared active modes. The dipole moment derivatives for the normal coordinates, $\partial\mu/\partial Q_i$, were taken from the works on the infrared absorption intensities,[14,15] and were transformed into those for the internal symmetry coordinates, $\partial\mu/\partial S_j$, by assuming a simplified relation

$$\partial\mu/\partial S_j = (\partial\mu/\partial Q_i)/L_{ji}, \tag{4}$$

where L_{ji} is the $\boldsymbol{L}$ matrix element connecting Q_i with S_j. The relation is exact for the ν_2 and ν_3 modes of carbon disulfide and the ν_3 mode of sulfur dioxide, but not for the ν_1 and ν_2 modes of sulfur dioxide. The exact transformation in terms of the $\boldsymbol{L}^{-1}$ matrix elements[16] cannot be applied to these two modes since

TABLE 1. INTRAMOLECULAR FORCE CONSTANTS (in mdyn·Å^{-1})[a]

	CS_2	SO_2
k_1	7.5	9.97
k_{12}	0.6	0.0
k_δ/l^2	0.234	0.81

a) Notations in Ref. 8 are used.

TABLE 2. PARAMETERS FOR THE NON-BONDED ATOM-ATOM INTERACTION

Atomic pair	A (kcal·Å/mol)	$B\times10^{-3}$ (kcal/mol)	C (Å^{-1})	Ref.
C···C	535	74.46	3.60	11
S···S	1430	220.8	3.62	12
O···O[a]	200	186.4	4.55	12

a) In calculation III′ for SO_2, the values of A and B were multiplied by 4.

the relative signs of $\partial\mu/\partial Q_1$ and $\partial\mu/\partial Q_2$ are not known. The symmetric stretching and the angle deformation modes of sulfur dioxide do not appreciably couple with each other, and the errors due to the approximation (4) are not serious for a crude estimation of splittings. The numerical values of the coupling constants and the related quantities are summarized in Table 3.

In calculation III, we adopted the potential including the terms due to the Coulomb interaction between the atomic charges as given by

$$V_{III} = V_{II}+\sum_{i,j} e_i e_j/r_{ij}, \tag{5}$$

where e_i and e_j denote the charges carried by the atoms i and j, respectively. The atomic charges for carbon disulfide and sulfur dioxide were so estimated as to reproduce the observed values of the electric quadrapole moment[17] and the dipole moment,[18] respectively; $e_C=-2e_S=0.58$ for the former and $e_S=-2e_O=0.46$ for the latter in the electronic charge unit.

The summation limit for the Coulomb terms in Eq. 5 was determined in two steps. When the atomic pairs to be included in the sum are selected directly by comparing the individual interatomic distances with a given threshold, the net charge under the summation sign does not generally vanish and a smooth convergence of the sum is not expected. Accordingly, we selected first appropriate molecular pairs by referring to the distances between the central atoms, and then picked up all the intermolecular atomic pairs involved in each of these molecular pairs. For the critical distance to be used for the selection of the molecular pairs, several values between 20 and 50 Å were tested, and the distance of 40 Å was found to be large enough to secure a convergent sum.

In order to confirm the consistency between the adopted model potential and the observed heats of sublimation, the values of the potential functions V_I and V_{III} were calculated for the equilibrium structure. They were then corrected for the crystal zero-point energies by using the average Debye temperature.[19] The value of V_{II} is the same as that of V_I at the equilibrium where the transition dipole terms do not contribute to the energies. The numerical calculation was carried out on a FACOM 230-75 computer at the Data Processing Center, Kyoto University.

Results and Discussion

Carbon Disulfide. According to X-ray analysis, the crystal of carbon disulfide belongs to the space group $D_{2h}{}^{18}$-C_{mca}, two molecules being contained in the Bravais unit cell.[9] The calculated and the observed values of the vibrational frequencies and the heat of sublimation are given in Table 4. Based on the

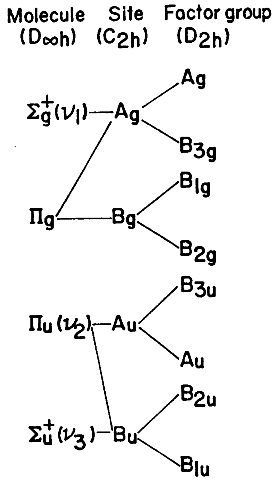

Fig. 1. Correlation diagram for vibrations of CS_2 crystal.

TABLE 3. DIPOLE MOMENT DERIVATIVES, L MATRIX ELEMENTS AND INTERMOLECULAR COUPLING CONSTANTS

	Mode(ν_i)	Internal symmetry coordinate (S_j)[a]	$\lvert\partial\mu/\partial Q_i\rvert$[b]	$\lvert L_{ji}\rvert$[c]	$\lvert\partial\mu/\partial S_j\rvert$[d]	$K_j{}^{ab}$[e]
CS_2	ν_2	$S_3=\Delta\phi$(in bc-plane)	20.12	0.4040	0.6418	0.0002[f]
	ν_3	$S_2=(\Delta r_1-\Delta r_2)/\sqrt{2}$	287.2	0.4446	8.3221	0.0318
SO_2	ν_1	$S_1=(\Delta r_1+\Delta r_2)/\sqrt{2}$	60.5	0.2794	2.7899	−0.0050
	ν_2	$S_2=\Delta\phi$	63.6	0.3037	2.6982	−0.0047
	ν_3	$S_3=(\Delta r_1-\Delta r_2)/\sqrt{2}$	165.9	0.3299	6.4791	0.0393

a) Δr_1 and Δr_2 are the two stretching coordinates and $\Delta\phi$ is the angle deformation coordinate. b) In esu·g$^{-1/2}$. c) In amu$^{-1/2}$ for ν_1 and ν_3, and in amu$^{-1/2}$·Å^{-1}·rad for ν_2 d) In debye·Å^{-1} for ν_1 and ν_3, and in debye·rad^{-1} for ν_2. e) In mdyn·Å^{-1} for ν_1 and ν_3, and in mdyn·Å·rad^{-2} for ν_2. f) For $S=\Delta\phi$(out of bc-plane), $K_4{}^{ab}$ was calculated to be 0.0003 mdyn·Å·rad^{-2}.

Table 4. Vibrational frequencies (in cm^{-1}) and heat of sublimation (in kcal/mol) of carbon disulfide crystal

		Obsd	Calcd		
			I	II	III
Internal modes					
ν_1	A_g	654[a]	656.3	656.6	655.8
	B_{3g}		656.4	656.4	656.6
ν_2	A_u		402.4	402.1	391.0
	B_{1u}	388.7[b]	400.8	400.5	394.8
	B_{2u}	400.1[b]	400.1	400.4	406.5
	B_{3u}	393.4[b]	402.2	402.6	399.9
ν_3	B_{1u}	1495[a]	1521.7	1507.6	1507.8
	B_{2u}	1528[a]	1521.5	1535.5	1538.8
External modes					
	A_g	73[a]	53	53	55
	B_{1g}		43	44	38
	B_{2g}		53	50	48
	B_{3g}	83[a]	54	53	62
	A_u		24	21	27
	B_{1u}	66[c]	56	56	59
	B_{2u}	66[c]	56	55	50
Heat of sublimation		9.02[d]	4.64	4.64	5.98

a) Ref. 20. b) Ref. 15. c) Ref. 21. d) Ref. 19.

correlation diagram (Fig. 1), the factor group splitting is expected for all the fundamentals, ν_1, ν_2 and ν_3. For the originally degenerate mode ν_2, the site group splitting is also expected. In the observed spectra,[15,20] ν_1 shows no splitting, while ν_2 and ν_3 split into as many components as expected theoretically. No empirical assignment of each component to proper symmetry species has been made because of the difficulty in measuring the low-temperature spectra of oriented crystals. The splittings could not be reproduced by calculation I which includes only the short range nonbonded atom-atom interaction terms (Table 4). Calculation I failed also in predicting the rotatory lattice frequencies[20] and the heat of sublimation,[19] but gave a fairly reasonable result for the translatory lattice modes.[21]

In calculation II, the intermolecular coupling constants K_2^{ab}, K_3^{ab} and K_4^{ab} were introduced between each molecule and its nearest neighbors lying on a common layer parallel to the bc plane. Since the ν_3 band in the infrared spectrum is very strong, splitting in the range 30—50 cm^{-1} observed for this band has been attributed to the interaction between the transition dipoles associated with the ν_3 mode.[15,20] In agreement with this interpretation, calculation II reproduced the observed splitting of the ν_3 mode satisfactorily. On the other hand, the ν_2 band in the infrared spectrum is very weak and the interaction between the transition dipoles is hardly expected to cause the observed splitting of the ν_2 mode.[15] Actually, the coupling constants K_3^{ab} and K_4^{ab} estimated from the infrared band intensity was found to give only one-tenth as large a splitting as the observed. For the lattice frequencies, calculations I and II gave almost the same results, since the dipole-dipole coupling terms affect only the intramolecular modes in which the internal coordinates appearing in those terms vibrate appreciably.

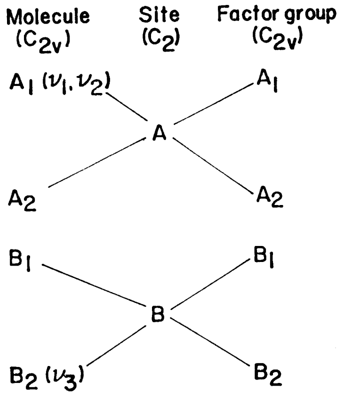

Fig. 2. Correlation diagram for vibrations of SO_2 crystal.

As shown in Table 4, all the observed factor group and site group splittings were reproduced very well by calculation III. The long range Coulomb interaction exerts little effect on ν_3, for which the splitting has been explained to be due to the transition dipole interaction, but gives rise to the splitting of ν_2 into three components appearing at intervals of about 5 cm^{-1} just as in the observed spectrum. Addition of the Coulomb terms to the intermolecular potential does not much affect the lattice frequencies, but improves the heat of sublimation appreciably.

Sulfur Dioxide. A number of split bands have been observed in the infrared and Raman spectra of sulfur dioxide crystal, and have been interpreted in terms of the factor group splittings, the summation bands and the bands of the isotopic species $^{34}SO_2$.[22-24] According to the correlation diagram (Fig. 2), the factor group splitting of ν_3 is expected in both the infrared and Raman spectra while that of ν_1 and ν_2 only in the Raman spectrum. The calculated and the observed values of the vibrational frequencies and the heat of sublimation are listed in Table 5.

As in the case of carbon disulfide, none of ν_1, ν_2 and ν_3 is calculated to split appreciably when only the short range forces are taken into account (calculation I), whereas the observed splittings are 4 cm^{-1} for ν_1 and 18 cm^{-1} for ν_2.[24] The splitting of ν_3 is estimated to be between 10 and 30 cm^{-1} from the Raman spectrum at 77 K in which three peaks assignable to ν_3 appear in the region around 1300 cm^{-1}.[24] If the splittings of ν_1 and ν_2 are assumed to arise from the interaction between the transition dipoles, the high- and low-frequency components for each mode are attributed to the A_2 and the A_1 species, respectively, by using Eq. 3 with properly chosen vectors $\boldsymbol{e}_a$, $\boldsymbol{e}_b$ and $\boldsymbol{R}$. The result agrees with the assignment by Anderson and Savoie[24] based on a comparison of the infrared and Raman frequencies.

In calculation II, three coupling constants K_1^{ab}, K_2^{ab} and K_3^{ab} were introduced, each molecule being assumed to interact with the neighboring four molecules lying on a common layer parallel to the ac plane.

Table 5. Vibrational frequencies (in cm^{-1}) and heat of sublimation (in kcal/mol) of sulfur dioxide crystal

		Obsd	Calcd			
			I	II	III	III′
Internal modes						
ν_1	A_1	1144[a]	1169.0	1167.7	1167.3	1169.6
	A_2	1148[a]	1169.7	1171.0	1170.6	1174.4
ν_2	A_1	524[a]	522.0	519.1	517.9	524.0
	A_2	542[a]	520.7	523.5	522.8	529.3
ν_3	B_1	1312[a]	1358.8	1348.1	1348.0	1350.2
	B_2	1324[a]	1358.2	1368.8	1369.6	1371.0
External modes						
	A_1	74[a]	42	42	34	60
	A_2		64	74	73	112
		67[a]	37	37	49	72
	B_1	160[b]	106	106	99	148
		101[b]	56	56	58	97
		67[b]	22	22	43	59
	B_2	141[b]	100	100	99	144
		101[b]	60	60	69	107
		67[b]	45	45	40	59
Heat of sublimation						
		8.91[c]	3.44	3.44	4.39	8.98

a) Ref. 24. b) Ref. 25. c) Ref. 19.

As shown in Table 5, the calculated splittings for ν_1 and ν_3 agree well with the observed ones, but not so for ν_2. In contrast to the case of carbon disulfide, addition of the Coulomb terms to the intermolecular potential of sulfur dioxide was found to give little effect on the magnitude of the factor group splittings, the discrepancy for ν_2 being left unreduced in calculation III. In order to obtain a satisfactory fit between the calculated and the observed splittings, it seems necessary to use more elaborate model potentials, for example by introducing polarizable charges.

The lattice frequencies and the heat of sublimation obtained in calculations I through III are far less than the observed values.[19,24,25] After several trials, the difficulty was overcome, without appreciable changes in the factor group splittings, by using about four times as large values of the parameters A and B for the O···O contact as those in calculations I, III and II (calculation III′, Table 5). Probably, the enhanced potential parameters do not faithfully represent the true feature of the non-bonded O···O interaction, but involve implicitly effects of some unknown interactions not considered herewith in this work.

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