Collision selection rules for asymmetric-top molecules

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Collision selection rules are found for asymmetric-top molecules. These rules explain the anomalies in the concentration dependence of the rotational-relaxation times in a D_2O–Ar mixture.

The point symmetry of a molecule imposes certain restrictions on the form of the generalized multipole expansions of the interaction potential and the scattering matrix of nonspherical molecules, giving rise to collision selection rules.[1] For symmetric-top molecules these rules were found in Ref. 2. Collision selection rules make it possible to describe experiments on the inelastic scattering of polar molecules by resonant radioscopic methods,[3] experiments on rotational relaxation,[4] and experiments involving the manifestations of the torque polarization which arises in a molecular gas with macroscopic gradients.[5]

In the present paper we work from the collision selection rules to explain the anomalies observed in Ref. 6 in the concentration dependence of the rotational-relaxation times of level populations for the D_2O–Ar molecular vapor mixture. The anomalous aspects of the behavior is that in the case of IR absorption at the 2_0–2_2 and 2_{-2}–2_0 transitions the corresponding relaxation time turns out to be independent of the Ar partial pressure. When the Ar partial pressure is significantly higher than that of the D_2O vapor, this behavior can evidently be explained most naturally on the basis that the relaxation of the 2_0 level occurs by transitions which are allowed only by molecule-molecule collisions.

Bakastov *et al.*[6] attributed the anomaly which they observed to the presence of two subsystems of levels in the rotational spectrum of the water molecule (for its para- and ortho-modifications). The 2_0 level should belong to one of these subsystems, while the 2_2, 2_{-2}, and 1_0 levels should belong to the other. It was later suggested that an exchange of rotational quanta between the level subsystems is possible only for molecule-molecule collisions.

In connection with Ref. 6 we might cite Ref. 7 where the existence of level subsystems in the D_2O spectrum was concluded from an analysis of the quasiequilibrium distribution of the populations of rotational states of the D_2O molecule in mixtures with Ar as these gas mixtures were cooled during flow through a Laval nozzle.

Collision selection rules derived in Refs. 8 and 9 confirm the existence of subsystems of levels in the rotational spectrum of the D_2O molecule. These studies dealt with molecule-atom collisions and took into account, along with the behavior of the interaction potential under transformations of the point symmetry group, the parity conservation law of a closed system. By analogy with the case of a diatomic molecule, the parity of the rotational level was taken to be $(-1)^J$, where J is the rotational quantum number. It is easy to see, however, that to introduce the parity in this phenomenological way runs into a contradiction with experimental data on absorption in the rotational spectrum of the D_2O molecule.[6]

In the present paper we explain the results of Refs. 6 and 7 with the help of selection rules obtained through a direct calculation of the functional dependence on the angles in the matrix elements of the scattering matrix. By themselves, the symmetry of the interaction under transformations of the point group and the invariance under coordinate inversion do not explain why the exchange of rotational quanta between the subsystems in molecule-atom collisions is forbidden. In this connection we find an additional symmetry property of the interaction, which is expressed in the existence of this restriction.

Following Ref. 2, we write the nonspherical D_2O–Ar interaction potential as the generalized multipole expansion

$$U(\mathbf{r},\omega)=\sum_{l} V_l(r)\sum_{mp}\beta_{lp}D_{mp}{}^{l}(\omega)Y_{lm}{}^{*}(\mathbf{r}), \tag{1}$$

where $D_{mp}{}^{l}(\omega)$ is the Wigner D function, which depends on the three Euler angles $\omega\equiv\varphi,\theta,\psi$; $Y_{lm}(\mathbf{r})$ is a spherical harmonic, which depends on the orientation of the radius vector ($\mathbf{r}$) connecting the centers of mass of the colliding particles; and the factors β_{lp} are chosen in such a manner that the potential (1) would not change under transformations of the point symmetry group of the D_2O molecule. According to Ref. 1, for nonvanishing factors β_{lp} we have

$$p=2\varkappa,\quad \varkappa=0,\ \pm1,\ \pm2;\quad \beta_{l-p}=\beta_{lp}. \tag{2}$$

The D_2O–D_2O interaction potential can be written in an analogous way as the expansion

$$U(\mathbf{r},\omega,\omega_1)=\sum_{ll_1L} V_{ll_1L}(r)\sum_{mpm_1p_1}\beta_{lp}D_{mp}{}^{l}(\omega)\beta_{l_1p_1}D^{l}_{m_1p_1}(\omega_1)$$
$$\times\langle lml_1m_1|LM\rangle Y_{LM}{}^{*}(\mathbf{r}), \tag{3}$$

where the subscript 1 specifies the molecular partner in the collision, $\langle lml_1m_1|LM\rangle$ is a Clebsch-Gordan coefficient, and the quantities $V_{ll_1L}(r)$ have the following properties:

$$\begin{aligned}&V_{ll_1L}(r)=0\quad \text{for}\quad l+l_1+L\ \ \text{odd},\\&V_{ll_1L}(r)=(-1)^{L}V_{l_1lL}(r)\ .\end{aligned}\tag{4}$$

We rewrite expansion (1) and (3) in a form which takes into account the symmetry of the interaction under coordinate inversion (I). We find

$$U(\mathbf{r},\omega)=\frac{1}{2}\,(U+U^{I})=\sum_{l}V_l(r)t_l^{(+)},$$

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$$U(\mathbf{r},\omega,\omega_1)=\frac{1}{2}(U+U^I)=\sum_{ll_1L}V_{ll_1L}(r)\,[t_{ll_1L}^{(+)}+t_{ll_1L}^{(-)}],\qquad(5)$$

where $t_l^{(+)}$ and $t_{ll_1L}^{(\pm)}$ are given by

$$t_l^{(+)}=\frac{1}{2}\sum_{mp}[\beta_{lp}+(-1)^p\beta_{l-p}]D_{mp}{}^l(\omega)\,Y_{lm}{}^*(\mathbf{r}),$$

$$t_{ll_1L}^{(+)}=\frac{1}{4}\sum_{pp_1mm_1}[\beta_{lp}+(-1)^p\beta_{l-p}]D_{mp}{}^l(\omega)\,[\beta_{l_1p_1}+(-1)^{p_1}\beta_{l_1-p_1}]$$

$$\times D_{m_1p_1}^{l_1}(\omega_1)\langle lml_1m_1|LM\rangle Y_{LM}{}^*(\mathbf{r}),\qquad(6)$$

$$t_{ll_1L}^{(-)}=\frac{1}{4}\sum_{pp_1mm_1}[\beta_{lp}-(-1)^p\beta_{l-p}]D_{mp}{}^l(\omega)\,[\beta_{l_1p_1}-(-1)^{p_1}\beta_{l_1-p_1}]$$

$$\times D_{m_1p_1}^{l_1}(\omega_1)\langle lml_1m_1|LM\rangle Y_{LM}{}^*(\mathbf{r}).$$

We note in connection with these expression that the combination $[\beta_{lp}-(-1)^p\beta_{l-p}]D_{mp}{}^l(\omega)$ arises in the multipole expansion of the interaction potential only in the case of a molecule-molecule interaction.

We construct the eigenfunctions of the rotational Hamiltonian of the D_2O molecule by means of combinations of the type[10]

$$\langle\omega|\psi_{JMKp}\rangle=i^J\left(\frac{2J+1}{16\pi^2}\right)^{1/2}[D_{MK}{}^J(\omega)+pD_{M-K}^J(\omega)],$$

$$p=\operatorname{sign}K,\qquad(7)$$

where $J=0,1,2,\ldots$; $M=-J,-J+1,\ldots,J$; $K=0,\pm1,\pm2,\ldots,\pm J$; and $p=\pm1$. According to the behavior attributed in molecular spectroscopy[11] to the Wigner D function under inversion, the parity S of the combination $\langle\omega|\psi_{JMKp}\rangle$ is $(-1)^{J-K}p$. The wave functions of the D_2O molecule for $J=1,2$ are listed in Table I for the case in which the z' axis of the coordinate system bound to the molecule coincides with the C_2 symmetry axis and is the axis of the intermediate moment of inertia. In this table we have used the functions $\langle\omega|JK\rangle\equiv i^JD_{MK}{}^J(\omega)$. The classification of the rotational states by symmetry types corresponds to the irreducible representations of the rotational subgroup of the point symmetry group of the molecule. The number of irreducible representations of the rotational symmetry subgroup is equal to the number of different molecular modifications, which, as we know, do not convert into each other in molecular collisions and which have a different resultant nuclear spin. The index $\tau=-J,-J+1,\ldots,J$ specifies the particular level of the rotational multiplet. The parity of the rotational functions of the D_2O molecule listed in Table I was found in accordance with the dipole absorption at the 1_0–2_{-2}, 2_0–2_{-2}, and 2_2–2_0 transitions in Ref. 6.

It was shown in Ref. 2 that in order to derive selection rules it is necessary to find the matrix elements of the expressions $t_l^{(+)}$ and $t_{ll_1L}^{(\pm)}$, "renormalizing" the nonspherical indices, $l\to f$ or $ll_1L\to ff_1F$. In calculating the matrix elements it is sufficient to use the functions $\langle\omega|\psi_{JMKp}\rangle$. For the quantities $g_f^{(\pm)}$, which determine the selection rules in molecule-atom and molecule-molecule collisions, we have

$$g_f^{(\pm)}=[1\pm pp'(-1)^{f+\Delta J+\Delta K}][\beta_{f\Delta K}\pm(-1)^{\Delta K}\beta_{f-\Delta K}]$$

$$\times J'K'J-K|f\Delta K\rangle$$

$$+[p\pm p'(-1)^{f+\Delta J+\Delta K}][\beta_{f\Sigma K}\pm(-1)^{\Delta K}\beta_{f-\Sigma K}]\langle J'K'JK|f\Sigma K\rangle,$$

$$\Delta K=K'-K,\quad \Sigma K=K'+K.\qquad(8)$$

It is easy to see that the first factors in both terms of this expression conserve the parity of the closed system. For the case of molecule-atom scattering, for example, according to the definition adopted for the parity of the rotational level we have

$$(-1)^{L+J-K}p=(-1)^{L'+J'-K'}p',\qquad(9)$$

where L is the orbital parity (the index of the spherical harmonic which arises in the corresponding plane-wave expansion). The indices with primes correspond to the quantum numbers of the state of the molecule after the collision. Using the well-known properties of an integral of a product of three spherical harmonics, we find the following selection rule for the orbital parity in molecule-atom scattering:

$L+L'+f$ – is even. $\qquad(10)$

Using (9) and (19), we find the condition

$$pp'(-1)^{f+\Delta J+\Delta K}=1,\qquad(11)$$

in complete accordance with the behavior of expression (8).

Using (2) and (8) for molecule-atom collisions, we find the selection rules

TABLE I.

J	τ	Wave function	Symmetry type	S	p
1	+1	$\frac{1}{\sqrt{2}}\left\{\lvert 11>+\lvert 1-1>\right\}$	B	+1	+1
	0	$\lvert 10>$	A	−1	+1
	−1	$\frac{1}{\sqrt{2}}\left\{\lvert 11>-\lvert 1-1>\right\}$	B	−1	−1
2	+2	$0.592\lvert 20>+0.806\{\lvert 22>+\lvert 2-2>\}$	A	+1	+1
	+1	$\frac{1}{\sqrt{2}}\left\{\lvert 21>+\lvert 2-1>\right\}$	B	−1	+1
	0	$\frac{1}{\sqrt{2}}\left\{\lvert 22>-\lvert 2-2>\right\}$	A	−1	−1
	−1	$\frac{1}{\sqrt{2}}\left\{\lvert 21>-\lvert 2-1>\right\}$	B	+1	−1
	−2	$0{,}806\lvert 20>-0.592\{\lvert 22>+\lvert 2-2>\}$	A	+1	+1

$$pp'(-1)^{f+\Delta J}=1, \quad \Delta K=2\varkappa, \quad \varkappa=0,\ \pm1,\ \pm2. \tag{12}$$

No additional selection rules arise for molecule-molecule collisions in this case since $g_f^{(-)}$ vanishes. Assuming that the multipole expansion of the scattering matrix converges rapidly, we retain in this expansion the first nonvanishing term, with $f=1$. According to (12) we then find that the following collisional transitions are forbidden in the lower part of the rotational spectrum:

$$1_0-2_0, \quad 2_{-2}-2_2; \tag{13}$$

the transitions 2_2–2_0 and 2_0–2_{-2} are allowed. This result applies to both molecule-atom and molecule-molecule collisions.

We believe that the reason for this discrepancy with experiment is as follows. The rotational Hamiltonian of an asymmetric top has off-diagonal matrix elements between states differing in the sign of K (for $K=1$). For this reason, the wave functions of an asymmetric top contain a superposition of states with positive and negative values of K, i.e., states with molecular rotation axes in different directions. If we use the semiclassical approximation to calculate the spectrum,[12] we can show that this mixing is a consequence of a tunneling between two classically allowed energy regions with $K \lessgtr 0$. When multipole expansion (1) and (3) are used, we again find off-diagonal elements between states differing in the sign of K. At $K \gg 1$, however, the matrix elements $\langle K|t_f^{(+)}|-K\rangle$ and $\langle K|t_{ff_1F}^{(\pm)}|-K\rangle$ are small in magnitude, while the expansions converge rapidly. For the general case we need a description of transitions involving a change in the sign of K which does not depend on the corresponding convergence rate of the multipole expansions. We correspondingly introduce the Hermitian operator $\hat{R}$, which sends the state $|K\rangle$ into the state $|-K\rangle$, and in expansions (1) and (3) we replace the combinations $\beta_{lp}D^{l}_{mp}(\omega)$ by the combinations $\beta_{lp}\{\hat{R}D_{mp}{}^{l}(\omega)\}$, where $\{AB\}=(AB+BA)$. Instead of $g_f^{(\pm)}$ we find

$$\tilde{g}_f^{(+)}=(p+p')\,g_f^{(+)} \tag{14a}$$

for molecule-atom scattering and

$$\tilde{g}_f^{(\pm)}=(pp_1+p'p_1')\,g_f^{(\pm)} \tag{14b}$$

for molecule-molecule scattering. It can be seen from (14) that in the case of molecule-atom collisions with $K \leftrightarrow -K$ tunneling collisional transitions the following selection rule must hold:

$$pp'=1. \tag{15}$$

On the other hand, for molecule-molecule collisions there are, in addition to the transitions for which selection rule (15) holds, transitions which satisfy the following selection rules;

$$pp'=-1, \quad p_1p_1'=-1. \tag{16}$$

These selection rules are not linked to the point symmetry of the molecule. For molecule-atom collisions these rules forbid transitions between levels for which the wave functions differ in the value of p. In particular, the following transitions are forbidden in the lower part of the spectrum:

$$2_0-1_0, \quad 2_2-2_0, \quad 2_0-2_{-2}\ , \tag{17}$$

in complete agreement with experiment. For molecule-molecule collisions, on the other hand, this restriction is not imposed and the selection rules are determined by the properties of the quantities $g_f^{(\pm)}$. We note in this connection that these selection rules rule out transitions beteween levels whose wave functions tranform in accordance with different irreducible representations of the rotational subgroup of the symmetry point group, i.e., for different molecule modifications of the D_2O molecule.

We also note that the tunneling collisional transitions $K \leftrightarrow -K$ could be interpreted as follows: The operator $\hat{R}$ introduced above is the same as the operator which performs a reflection in a plane passing through the axis of the top. This reflection changes the relative positions of the axes of the coordinate system bound to the molecule, since a transformation from a left-handed to a right-handed coordinate system occurs. Incorporating the operator $\hat{R}$ in the interaction causes an "averaging" over the right-handed and left-handed coordinate systems; after this averaging the interaction acquires some new symmetry properties, which are expressed in selection rules (15) and (16).

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[1] V. D. Borman, A. S. Bruev, L. A. Maksimov, and B. I. Nikolaev, Teor. Mat. Fiz. **13**, 241 (1972).

[2] V. D. Borman, A. S. Bruev, L. A. Maksimov, and B. I. Nikolaev, Zh. Eksp. Teor. Fiz. **72**, 2100 (1977) [Sov. Phys. JETP **45**, 1103 (1977)].

[3] J. Steinfeld and P. Houston, in: Laser and Coherent Spectroscopy (Russ. transl. Mir, Moscow, 1982, p. 11).

[4] E. D. Bulatov, E. A. Vinogradov, V. K. Konyukhov, *et al.*, Zh. Eksp. Teor. Fiz. **76**, 543 (1979) [Sov. Phys. JETP **49**, 274 (1979)].

[5] A. S. Bruev, Zh. Eksp. Teor. Fiz. **74**, 2027 (1978) [Sov. Phys. JETP **47**, 1054 (1978)]; A.S. Bruev, in: Molekulyarnaya gazodinamika (Molecular Gasdynamics), Nauka, Moscow, 1982, p. 194.

[6] S. S. Bakastov, V. K. Konyukhov, and V. I. Tikhonov, Pis'ma Zh. Eksp. Teor. Fiz. **37**, 427 (1983) [JETP Lett. **37**, 506 (1983)].

[7] V. I. Tikhonov, in: Twelfth International Symposium on Rarefield Gas Dynamics. Book of Abstracts, Novosibirsk, 1982, p. 496.

[8] V. I. Selyakov, Zh. Prikl. Mekh. Tekh. Fiz. **3**, 10 (1980).

[9] V. K. Konyukhov, Kratk. Soobshch. Fiz. No. 10, 20 (1982).

[10] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika, Nauka, Moscow, 1974, p. 475 (Quantum Mechanics, Pergamon Press, Oxford, 1977).

[11] E. P. Wigner, Theory of Groups and Its Application to the Quantum Mechanics of Atomic Spectra, Academic Press, New York (1959) (Russ. transl. IIL, Moscow, 1961, p. 258).

[12] P. A. Braun and A. A. Kiselev, Vvedenie v teoriyu molekulyarnykh spektrov (Introduction to the Theory of Molecular Spectra), Izd. LGU, Leningrad, 1983, p. 105.

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