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Effect of Nuclear Spin Correlations on the Scattering of Neutrons by Molecules

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The scattering of slow neutrons by spherical-top molecules is discussed taking into account the correlations in nuclear spin caused by the presence of identical nuclei in the molecule. Matrix elements for the scattering are evaluted between different symmetrized states using group-theoretical methods. It is shown that coherent scattering can cause only those transitions which leave the symmetry of the total molecular wave function unchanged, while incoherent scattering can cause transitions between states of different symmetry. Explicit expressions for the cross section for scattering from methane are derived. These are different from those obtained by Michael recently in a treatment of the same problem. Formulas for the cross section for symmetric-top molecules are also derived. Numerical calculations have been performed for the scattering of 0.025-eV neutrons through a 10° scattering angle by methane gas at 10 and 300°K. It is found, contrary to Michael's observations, that at 10°K nuclear-spin correlations produce considerable differences in the scattering compared with the case where their effects are ignored. At 300°K, however, their effects are negligible. These findings are in accord with the predictions made earlier by Zemach and Glauber.

I. INTRODUCTION

IT is well known[1] that in systems containing identical particles, the total wave function Ψ must transform into itself under a permutation of the identical particles if the particles obey Bose statistics, and to $(-1)^P\Psi$ if the particles obey Fermi statistics, where P is the order of the permutation. Applied to molecules containing identical nuclei, this restriction due to permutational symmetry results in a correlation between the space part and the spin part of the molecular wave function.[2,3] This in turn produces a correlation between the rotational angular momentum of the molecule and the total-spin angular momentum of the identical nuclei.[4] For example, if we consider hydrogen in its vibrational ground state, we find that the states of odd-J value (where J is the rotational quantum number) are associated with a total nuclear spin of 1 (orthohydrogen), while states of even J are associated with a nuclear spin of 0 (parahydrogen). Similarly, for methane we have the state $J=0$ associated with a total nuclear spin of 2 (metamethane), the state $J=1$ with a nuclear spin of 1

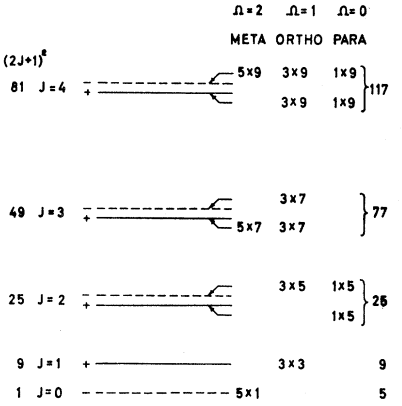

FIG. 1. A schematic drawing of the first few rotational levels of the methane molecule (in the ground vibrational state). The states marked + correspond to even parity, and those marked − correspond to odd parity. The − state arises as a result of inversion tunneling and, since the barrier to tunneling is very high, will lie very close to the + state associated with the same J value. The numbers on the right-hand side denote the multiplicities associated with a given J for various values of Ω, the total nuclear spin. The numbers on the left-hand side indicate the multiplicities in the absence of spin correlation.

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* Present address: Department of Physics, Iowa State University, Ames, Iowa.

[1] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Ltd., London, 1959).

[2] A. C. Zemach and R. J. Glauber, Phys. Rev. **101**, 129 (1956).

[3] See also Eugene P. Wigner, *Group Theory* (Academic Press Inc., New York, 1959), p. 257.

[4] We shall henceforth refer to this correlation simply as spin correlation. The situation where this correlation is ignored will be referred to as the uncorrelated case.

(orthomethane), etc. (see Fig. 1). The multiplicities of the rotational levels are altered as a result of spin correlations, and using the methods of group theory, Wilson[5] has calculated these for a number of molecules. We shall henceforth refer to the multiplicity factors calculated by Wilson as Wilson factors.

The question now arises as to how the intensities of the peaks due to the rotational transitions in neutron scattering will be modified by including the effects of permutational symmetry. The formal aspects of the problem have been briefly considered by Zemach and Glauber[2] in a fundamental paper (referred to hereafter as ZG). These authors show that apart from the modifications due to the altered multiplicites, the inclusion of spin correlations results in an extra contribution to the cross section. This extra contribution arises from the interference between the incoherent scatterings by the different identical nuclei in the molecule. Although the formal framework is available, most calculations[6–9] of neutron scattering by molecules have ignored spin-correlation effects presumably because of the remark made in the appendix of ZG that such effects are small for most molecules except at low temperatures. An exception is the case of hydrogen, which has been treated in detail by Sarma,[10] and by Young and Koppel.[11] Recently Stiller[12] has suggested that spin-correlation effects might not be negligible (for molecules other than hydrogen) and would have to be considered in making comparisons between theory and experiments. The situation regarding the effects of spin correlations on neutron scattering thus does not appear to be clear, with conflicting views expressed by Zemach and Glauber and by Stiller. The actual situation can be assessed only by performing a detailed numerical calculation. An effort in this direction has in fact been made by Michael[13] recently. Using the formalism of ZG, Michael attempted to take spin-correlation effects into account for the case of neutron scattering from methane gas by including the extra term mentioned earlier and weighting the thermal distribution over the initial states by the Wilson factors. Numerical calculations made by him for the scattering of 0.025-eV neutrons by a hypothetical methane gas at 10°K through a scattering angle of 10° showed that the partial differential cross section was changed at the most by about 5% from the uncorrelated value. Unfortunately, Michael's work seems to be based on an incorrect interpretation of the equation given in ZG, and we have therefore re-examined the problem. In this paper,[14] by considering the structure of the wave function when spin correlations are present, we show that Michael's approach is incorrect, and that the thermal average of the neutron scattering matrix element cannot be obtained by simply considering the element in the uncorrelated case and weighting it by the Wilson factor. Using group-theoretical methods, we derive general expressions for neutron scattering by spherical-top molecules containing identical nuclei, under the usual assumptions of no rotation-vibration interaction and independent averaging over orientations for the rotational and vibrational matrix elements. For simplicity, we make the further assumption that there is only one class of identical nuclei in the molecule, and that the permutation group of such nuclei is isomorphous with the point group of the molecule. The results can, if necessary, be generalized to more complex cases. The selection rules for transitions between (spatial) states of different symmetry are derived, and explicit formulas are obtained for the scattering of slow neutrons by methane gas. Using these formulas, numerical calculations have been made for the situation considered by Michael, and it is shown that there are important modifications to the scattering cross section compared with those obtained in the uncorrelated case. The calculations have been repeated for 300°K and it is observed that at the higher temperature, the influence of spin correlation is much less, as was indeed anticipated by Zemach and Glauber.

The formulas derived have been extended to the case of scattering by symmetric-top molecules like ammonia. Some other applications are also briefly indicated.

II. MATHEMATICAL FORMULATION

A. Spherical-Top Molecule

We wish to discuss in this section the scattering of slow neutrons by a gas of spherical-top molecules taking spin correlations into account. As already mentioned in Sec. I, we shall assume that there is only one class of identical nuclei within the molecule and that the permutation group $\mathcal{P}$ of the identical nuclei is isomorphous with the point group of the molecule.

It is known[2,15] that the scattering can be very generally discussed in terms of the intermediate scattering function $I(\mathbf{Q},t)$ defined by

$$I(\mathbf{Q},t)=\sum_{\nu\mu}\langle\Psi|\,a_\nu a_\mu \exp[i\mathbf{Q}\cdot\mathbf{r}_\nu(t)] \times\exp[-i\mathbf{Q}\cdot\mathbf{r}_\mu(0)]\,|\,\Psi\rangle_T. \quad (1)$$

Here a_ν and a_μ denote the spin-dependent scattering lengths of the nuclei ν and μ, and $\hbar\mathbf{Q}$ the gain in mo-

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[5] E. B. Wilson, J. Chem. Phys. **3**, 276 (1935).

[6] A. Rahman, J. Nucl. Energy Pt. **A13**, 128 (1961).

[7] T. J. Krieger and M. Nelkin, Phys. Rev. **106**, 290 (1957).

[8] G. W. Griffing, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. I, p. 435.

[9] Sidney Yip, Ph.D. thesis, University of Michigan, 1962 (unpublished).

[10] G. Sarma, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1960), p. 397.

[11] J. A. Young and J. U. Koppel, Phys. Rev. **135**, A603 (1964).

[12] H. Stiller, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. I, p. 468. See also S. Hautecler and H. Stiller, *ibid.*, p. 423.

[13] P. Michael, Phys. Rev. **138**, A692 (1965).

[14] A brief account of this work was presented at the Symposium on the Inelastic Scattering of Neutrons by Condensed Systems, Brookhaven, 1965 (unpublished).

[15] A. C. Zemach and R. J. Glauber, Phys. Rev. **101**, 118 (1956).

mentum of the neutron. The bracket $\langle\cdots\rangle_T$ indicates a thermal average. The operator $\mathbf{r}$ is a Heisenberg operator defined by

$$\mathbf{r}(t)=e^{iHt/\hbar}\mathbf{r}e^{-iHt/\hbar},$$

where H is the Hamiltonian of the system. The partial differential cross section may then be written in terms of the intermediate scattering function as

$$\frac{d^2\sigma}{d\Omega dE}=\frac{1}{2\pi\hbar}\frac{k}{k_0}\int e^{-i\omega t}I(\mathbf{Q},t)dt, \qquad (2)$$

where $\hbar\omega$ is the energy transferred to the neutron, and k_0 and k are the magnitudes of the wave vectors of the incident and scattered neutrons, respectively.

In the presence of spin correlations, it is shown in ZG that

$$I(\mathbf{Q},t)=\langle\Psi|\sum_{\substack{\nu\mu\\ \text{all}\\ \text{nuclei}}}A_\nu A_\mu f_{\nu\mu}|\Psi\rangle_T+\langle\Psi|\sum_{\substack{\nu\\ \text{all}\\ \text{nuclei}}}C_\nu^2 f_{\nu\nu}|\Psi\rangle_T + \sum_{\substack{\nu\mu\\ \nu\neq\mu,\\ \text{identical}\\ \text{nuclei}}}C_\nu^2\langle\Psi|f_{\nu\mu}Z(\Omega)|\Psi\rangle_T. \qquad (3)$$

In Eq. (3), A_ν and C_ν denote, respectively, the coherent and incoherent scattering amplitudes; $f_{\nu\mu}$ stands for the operator $\exp[i\mathbf{Q}\cdot\mathbf{r}_\nu(t)]\exp[-i\mathbf{Q}\cdot\mathbf{r}_\mu(0)]$; and $Z(\Omega)$ is given by

$$Z(\Omega)=\frac{\Omega(\Omega+1)-\eta S_\nu(S_\nu+1)}{S_\nu(S_\nu+1)\eta(\eta-1)},$$

with S_ν being the spin of each of the identical nuclei, η the number of identical nuclei in the molecule, and Ω the total nuclear spin of the molecule. It is to be emphasized that Ψ in Eq. (3) stands for the symmetrized total molecular wave function, i.e., a wave function which has the right symmetry properties with respect to the permutations of the identical nuclei, as discussed in the introduction. The last term in Eq. (3) is the extra contribution referred to earlier which vanishes in the uncorrelated case leaving only the first two terms of that equation, with Ψ now standing for the unsymmetrized total wave function.

To proceed further, we must take into account the detailed structure of Ψ. Toward this end, it is convenient to consider first the unsymmetrized form of Ψ, which, neglecting rotation-vibration interaction, can be written as a simple product of the electronic, translational, rotational, vibrational, and spin functions ψ_{el}, ψ_{t}, ψ_R, ψ_{v} and ξ, respectively, i.e.,

$$\Psi=\psi_{\text{el}}\psi_{\text{t}}\psi_R\psi_{\text{v}}\xi. \qquad (4)$$

Now the molecule will normally be in the electronic ground state both before and after the neutron-scattering process. The ground-state electronic function ψ_{el} is invariant under the permutations of identical nuclei and hence may be neglected in our further considerations. Regarding the remaining functions in Eq. (4), we note the following: In the first place ψ_{t} transforms according to the identity representation of $\mathcal{P}$. Secondly the rotational wave function is the well-known spherical-top wave function $\psi_K{}^{JM}$, where the labels M and K denote, respectively, the projection of J, the rotational quantum number, on a space-fixed axis and on an axis fixed in the molecule. As for the vibrational wave function, we can classify it according to the irreducible representations of $\mathcal{P}$, since the vibrational Hamiltonian is invariant under $\mathcal{P}$. We can therefore write it as $\psi_\beta{}^{VS}$, where S signifies which particular representation of a given type V, and β which row of this representation the wave function belongs to. The vibrational energy levels are thus classified by the pair of indices (V,S). Finally we observe that the spin function ξ is simply the product of the spin functions for each of the nuclei.

Since the molecular Hamiltonian as a whole is invariant under the permutations of identical nuclei, we can classify both the space part $\psi_{\text{t}}\psi_R\psi_{\text{v}}$ and the spin part ξ of Ψ in Eq. (4) in terms of the irreducible representation of $\mathcal{P}$. Let us denote the symmetrized spatial wave function constructed from the degenerate manifold $\psi_{\text{t}}\psi_K{}^{JM}\psi_\beta{}^{VS}$ [where β runs over all the rows of S, and K runs over the $(2J+1)$ values from $-J$ to $+J$] as $\phi(VSJMt;\lambda\alpha r)$. Here r indicates which particular representation of the type λ that the symmetrized function belongs to, and α denotes the row of that representation. In a similar fashion, since Ω is a good quantum number, we can classify the spin part ξ as $\xi(\Omega;\lambda'\alpha'r')$ with λ', α', and r' having meanings corresponding to the indices λ, α, r in ϕ. We can thus write the molecular wave function Ψ in the uncorrelated case as

$$\Psi=\phi(VSJMt;\lambda\alpha r)\xi(\Omega;\lambda'\alpha'r'), \qquad (5)$$

with the indices (λ,α,r) and (λ',α',r') being completely independent of each other. By using the wave function (5) in the first two terms of Eq. (3) and evaluating the thermal averages, we shall obtain the intermediate scattering function appropriate to the uncorrelated case. Actually it is unnecessary to use the function (5) for this purpose. One might just as well work with a molecular wave function expressed in terms of the reducible basis i.e., with

$$\Psi=\psi_{\text{t}}\psi_K{}^{JM}\psi_\beta{}^{VS}\xi, \qquad (6)$$

which is what has been done by Rahman, Griffing, and Yip to derive expressions for the scattering of neutrons by spherical-top molecules. The use of both Eq. (5) and Eq. (6) will give the same results, since the first two terms of Eq. (3) essentially involve traces of operators over manifolds of degenerate states, and these remain unaltered when we make a transformation from the basis (6) to the basis (5). Our object in writing Ψ in the form of Eq. (5) is mainly to draw attention to the important differences that arise when spin correlations are present.

When the effects of permutational symmetry on the *total* wave function are considered, Ψ cannot be written as in (5) but must be expressed in the form[2,3]

$$\Psi=(1/m_\lambda)^{1/2}\sum_{\alpha=1}^{m_\lambda}\phi(VSJMt;\lambda\alpha r)\xi(\Omega;\Lambda\alpha r'),\qquad(7)$$

where m_λ denotes the dimensionality of the irreducible representation λ.[16] The representations λ and Λ are no longer unrelated as in Eq. (5). In fact, if λ^* denotes the representation which is complex conjugate to λ, then Λ denotes the representation λ^* if the identical nuclei are bosons, and $(-1)^{P_\alpha}\lambda^*$ if the nuclei are fermions, where P_α stands for the order of the permutation α of $\mathcal{P}$. It can be shown[2] that the Ψ given in (7) transforms in the right manner under the operations of $\mathcal{P}$, and further that it is unique. The indices r and r' are, of course, independent.

We now introduce the wave function (7) into Eq. (3) and perform the integration over the spin parts and the summation over r'. We then obtain, writing

$$\phi(VSJMt;\lambda\alpha r)=|i\rangle$$

for simplicity,

$$I(\mathbf{Q},t)=\langle i|\sum_{\substack{\nu\mu\\ \text{all}\\ \text{nuclei}}}A_\nu A_\mu f_{\nu\mu}(1/m_\lambda)\sum_\Omega n_\Lambda(\Omega)|i\rangle_T+\langle i|\sum_{\substack{\nu\\ \text{all}\\ \text{nuclei}}}C_\nu^2 f_{\nu\nu}(1/m_\lambda)\sum_\Omega n_\Lambda(\Omega)|i\rangle_T$$
$$+\sum_{\substack{\nu\mu\\ \text{identical}\\ \text{nuclei}}}C_\nu^2\langle i|f_{\nu\mu}(1/m_\lambda)\sum_\Omega n_\Lambda(\Omega)Z(\Omega)|i\rangle_T-\sum_{\substack{\nu\\ \text{identical}\\ \text{nuclei}}}C_\nu^2\langle i|f_{\nu\nu}(1/m_\lambda)\sum_\Omega n_\Lambda(\Omega)Z(\Omega)|i\rangle_T,\qquad(8)$$

where $n_\Lambda(\Omega)$ denotes the number of times the representation Λ is contained in the basis of spin functions corresponding to total nuclear spin Ω. An expression analogous to the above equation has been deduced in ZG [see Eq. (2.9)] without specific reference to any particular type of molecule. This expression, which forms the starting point of Michael's work, is somewhat misleading in that it is not clearly stated that the matrix elements should be taken between *symmetrized* spatial states, and Michael has in fact taken the matrix elements between unsymmetrized states.[17] Michael's approach is equivalent to taking the terms involving Λ outside the matrix element in Eq. (8), and performing the summation over λ and Λ corresponding to a given degenerate manifold separately. This is clearly not possible since the representations λ and Λ are related, as stated above.

In order to deduce the selection rules, we now introduce the final states $\phi(V''S''J''M''t'';\lambda''\alpha''r'')=|f\rangle$, upon which Eq. (8) becomes

$$I(\mathbf{Q},t)=\sum_i P_{VSJt}(T)\frac{1}{m_\lambda}\sum_f\Big\{\Big[\sum_\Omega n_\Lambda(\Omega)\Big]\langle i|\sum_{\substack{\nu\\ \text{all}\\ \text{nuclei}}}A_\nu\exp[i\mathbf{Q}\cdot\mathbf{r}_\nu(t)]|f\rangle\langle f|\sum_\mu A_\mu\exp[-i\mathbf{Q}\cdot\mathbf{r}_\mu(0)]|i\rangle$$
$$+\Big[\sum_\Omega n_\Lambda(\Omega)Z(\Omega)\Big]\langle i|\sum_{\substack{\nu\\ \text{identical}\\ \text{nuclei}}}C_\nu\exp[i\mathbf{Q}\cdot\mathbf{r}_\nu(t)]|f\rangle\langle f|\sum_\mu C_\mu\exp[-i\mathbf{Q}\cdot\mathbf{r}_\mu(0)]|i\rangle$$
$$+\Big[\sum_\Omega n_\Lambda(\Omega)\Big]\sum_{\substack{\nu\\ \text{non-identical}\\ \text{nuclei}}}C_\nu^2\langle i|\exp[i\mathbf{Q}\cdot\mathbf{r}_\nu(t)]|f\rangle\langle f|\exp[-i\mathbf{Q}\cdot\mathbf{r}_\nu(0)]|i\rangle$$
$$+\Big[\sum_\Omega n_\Lambda(\Omega)(1-Z(\Omega))\Big]\sum_{\substack{\nu\\ \text{identical}\\ \text{nuclei}}}C_\nu^2\langle i|\exp[i\mathbf{Q}\cdot\mathbf{r}_\nu(t)]|f\rangle\langle f|\exp[-i\mathbf{Q}\cdot\mathbf{r}_\nu(0)]|i\rangle\Big\}.\qquad(9)$$

$P_{VSJt}(T)$ is the Boltzmann factor for the degenerate energy level specified by $(VSJt)$ and is given by

$$P_{VSJt}(T)=\frac{\exp(-E_{VSJt}/k_BT)}{\sum_{VSJt}n_{VSJt}\exp(-E_{VSJt}/k_BT)},\qquad(10)$$

where n_{VSJt} denotes the total multiplicity of the energy level $(VSJt)$ and is nothing but the Wilson factor for that level. E_{VSJt} represents the energy of the level concerned.

In Eq. (9), we observe that the operators in all the terms except the last are invariant under all operations of $\mathcal{P}$. From group theory[18] it follows, therefore, that the matrix elements in the first three terms vanish unless $\lambda=\lambda''$ and $\alpha=\alpha''$. The operators in the last term are not invariant and hence can cause transitions between states of different symmetry. It may thus be seen that only the incoherent scattering from the identical nuclei can cause such transitions. Although the selection rules given above have been deduced with special reference to the spherical-top molecule, they are in fact quite general.[2,14] Thus, in the case of the hydrogen molecule in the ground vibrational state, we have the well-known result[11] that coherent scattering can cause only transitions between states of the same total nuclear spin, i.e., ortho to ortho or para to para states, while incoherent

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[16] We have included a normalizing factor $(1/m_\lambda)^{1/2}$ which was omitted by Zemach and Glauber.

[17] Further, Michael has summed the Wilson factors over all possible symmetries of the vibrational states, whereas the assumption made later in his paper, following Griffing, is that the molecule is in its ground vibrational state before and after scattering.

[18] V. Heine, *Group Theory in Quantum Mechanics* (Pergamon Press, Inc., New York, 1960).

scattering can cause a spin-flip, i.e., ortho-to-para, transition.

Having derived the selection rules, we are still faced with the problem of evaluating the matrix elements between symmetrized spatial states in Eq. (8). For this purpose, we use the result proved in Appendix A, namely, that if O is any operator, and ψ_j are a set of functions forming the basis for a reducible representation of a group $\mathcal{P}$, then

$$\sum_{r\alpha}\langle\phi(\lambda\alpha r)|O|\phi(\lambda\alpha r)\rangle$$

$$=\sum_{R\in\mathcal{P}}\sum_{jj'}\frac{m_\lambda}{H}\chi^{*(\lambda)}(R)R_{j'j}\langle\psi_j|O|\psi_{j'}\rangle,\quad(11)$$

where H is the order of the group, and λ, α, r, and m_λ have the same meaning as before. $\chi^{(\lambda)}(R)$ is the character of R in the irreducible representation λ. $R_{j'j}$ is the reducible representation according to which the ψ_j must transform under $\mathcal{P}$. If λ is not contained at all in the reducible representation, (11) will identically vanish. In our case, the reducible basis $\psi_t\psi_K{}^{JM}\psi_\beta{}^{VS}$ transforms under the operation R of group $\mathcal{P}$ according to

$$R(\psi_t\psi_K{}^{JM}\psi_\beta{}^{VS})$$

$$=\sum_{K'\beta'}D_{K'K}{}^J(\bar{R})D_{\beta'\beta}{}^V(R)\psi_t\psi_{K'}{}^{JM}\psi_{\beta'}{}^{VS},\quad(12)$$

where $D_{\beta'\beta}{}^V(R)$ denotes the irreducible representation V, $\bar{R}$ is the pure rotation associated with the point group operation R, and $D_{K'K}{}^J(\bar{R})$ is the well-known rotation matrix of order J which may be calculated according to the formulas given in Rose.[19] We may note that $\bar{R}$ does not connect states with different M.[5]

Using Eqs. (11) and (12) in Eq. (8), we get for the first term (i.e., the intermediate scattering function for coherent scattering), for instance,

$$I_{\mathrm{coh}}(\mathbf{Q},t)=\sum_A(1/H)\chi^{*(\lambda)}(R)[\textstyle\sum_\Omega n_\Lambda(\Omega)]P_{VSJt}(T)$$

$$\times D_{K'K}{}^J(\bar{R})D_{\beta'\beta}{}^V(R)\langle\psi_t\psi_K{}^{JM}\psi_\beta{}^{VS}|$$

$$\times\textstyle\sum_{\nu\mu}A_\nu A_\mu f_{\nu\mu}|\psi_{\beta'}{}^{VS}\psi_{K'}{}^{JM}\psi_t\rangle.\quad(13)$$

The symbol A stands collectively for V, S, J, M, t, λ, R, β', β, K', and K. The matrix element in Eq. (13) connects unsymmetrized states and may therefore be evaluated by methods employed previously by Griffing.[8]

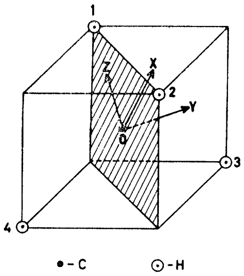

FIG. 2. Schematic drawing of the methane molecule. The body-fixed axes are also shown.

This involves factorizing the matrix element into a product of three matrix elements connecting respectively translational, rotational, and vibrational states. To do this we first write

$$\mathbf{r}_\nu=\boldsymbol{\varrho}+\mathbf{b}_\nu+\mathbf{u}_\nu,\quad(14)$$

where $\boldsymbol{\varrho}$ is the position of the center of mass of the molecule, $\mathbf{b}_\nu$ is the vector from the center of mass to the equilibrium position of the νth nucleus in the molecule, and $\mathbf{u}_\nu$ is the displacement of the nucleus from this position due to molecular vibrations.

We now make the following assumptions, as was done earlier by Griffing:

(1) There is no correlation between the translational motion and the rotations and vibrations. Further there is no correlation between the motion of nuclei in different molecules. This is permissible since we are considering a gas.

(2) The averaging over orientations of the molecule may be performed separately for the rotational and vibrational matrix elements. This assumption is necessary because the vibrational matrix element,

$$\langle\psi_\beta{}^{VS}|\exp[i\mathbf{Q}\cdot\mathbf{u}_\nu(t)]\exp[-i\mathbf{Q}\cdot\mathbf{u}_\mu(0)]|\psi_{\beta'}{}^{VS}\rangle,$$

and the rotational matrix element,

$$\langle\psi_K{}^{JM}|\exp[i\mathbf{Q}\cdot\mathbf{b}_\nu(t)]\exp[-i\mathbf{Q}\cdot\mathbf{b}_\mu(0)]|\psi_{K'}{}^{JM}\rangle,$$

both depend on molecular orientations. Actually Griffing does the averaging over orientations of the vibrational matrix element classically. The validity of this approximation of separate averaging for the rotational and vibrational parts, and further doing the averaging in the case of the vibrational part classically, has been discussed by Griffing.

Making use of these assumptions, Eq. (13) may be written as

$$I_{\mathrm{coh}}(\mathbf{Q},t)=N\sum_R\{(\textstyle\sum_\lambda\chi^{*(\lambda)}(R)\sum_\Omega n_\Lambda(\Omega))\langle\psi_t|\exp[i\mathbf{Q}\cdot\boldsymbol{\varrho}(t)]\exp[-i\mathbf{Q}\cdot\boldsymbol{\varrho}(0)]|\psi_t\rangle_T$$

$$\times\sum_{VSJ}P_{VSJ}(T)\sum_{\beta'\beta}(1/H)D_{\beta'\beta}{}^V(R)\sum_M\sum_{K'K}D_{K'K}{}^J(\bar{R})\langle\psi_\beta{}^{VS}\psi_K{}^{JM}|\textstyle\sum_{\nu\mu}A_\nu A_\mu\exp[i\mathbf{Q}\cdot(\mathbf{u}_\nu(t)+\mathbf{b}_\nu(t))]$$

$$\times\exp[-i\mathbf{Q}\cdot(\mathbf{u}_\mu(0)+\mathbf{b}_\mu(0))]|\psi_{K'}{}^{JM}\psi_{\beta'}{}^{VS}\rangle.\quad(15)$$

Here N is the number of molecules and the summations over ν and μ now run only over the nuclei in one molecule. The thermal average of the translational part has been separated out and the Boltzmann factor $P_{VSJ}(T)$ is given

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[19] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

TABLE I. Character table for point groups T_d and O and Wilson factors for the first few rotational levels of CH_4 in the ground vibrational state. $\chi_{SP}(R)$ and $\chi_J(R)$ denote the characters of the reducible representations generated by the spin and rotational wave functions, respectively. $n_\Lambda(\Omega)$ is as defined in the text, while $n_\lambda(J)$ is the number of times the irreducible representation λ is contained in the reducible representation corresponding to that J. $n_J{}^+$ and $n_J{}^-$ are the multiplicities for the even and odd parity levels corresponding to the various Ω (see Fig. 1). The Wilson factors are obtained by summing the contributions from the different Ω's.

T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	$n_\Lambda(\Omega)$			$\sum_\Omega n_\Lambda(\Omega)$	$n_\lambda(J)$				
O	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$	$\Omega=0$	$\Omega=1$	$\Omega=2$		$J=0$	$J=1$	$J=2$	$J=3$	$J=4$
A_1	1	1	1	1	1	0	0	5	5	1	0	0	0	9
A_2	1	1	1	−1	−1	0	0	0	0	0	0	0	7	0
E	2	−1	2	0	0	1	0	0	1	0	0	5	0	9
T_1	3	0	−1	−1	1	0	0	0	0	0	3	0	7	9
T_2	3	0	−1	1	−1	0	3	0	3	0	0	5	7	9
$\chi_{SP}(R)$	16	4	4	8	2									
$\chi_0(R)$	1	1	1	1	1									
$\chi_1(R)$	9	0	−3	−3	3									
$\chi_2(R)$	25	−5	5	5	−5									
$\chi_3(R)$	49	7	−7	−7	−7									
$\chi_4(R)$	81	0	9	9	9									

J / Ω	$n_J{}^+$					$n_J{}^-$				
	0	1	2	3	4	0	1	2	3	4
0	0	0	5	0	9	0	0	5	0	9
1	0	9	0	21	27	0	0	15	21	27
2	0	0	0	35	0	5	0	0	0	45
Wilson factor	0	9	5	56	36	5	0	20	21	81

by

$$P_{VSJ}(T)=\frac{\exp(-E_{VSJ}/k_BT)}{\sum_{VSJ} n_{VSJ}\exp(-E_{VSJ}/k_BT)}.$$

The vibrational and rotational parts are written together at this stage. Their separation will be carried out later. As mentioned previously, if the representation λ is not contained in the manifold of states ($VSJM$), then there is no contribution from this λ to $I_{\text{coh}}(\mathbf{Q},t)$. We can therefore formally allow λ to run over all the irreducible representations of $\mathcal{P}$ and thus do the sum $\sum_\lambda \chi^{*(\lambda)}(R)\sum_\Omega n_\Lambda(\Omega)$ separately. This is of great use in actual computations.

Similar expressions may be derived for the other contributions to the intermediate scattering function in Eq. (9) by substituting C_ν for A_ν and $\sum_\Omega Z(\Omega)n_\Lambda(\Omega)$ for $\sum_\Omega n_\Lambda(\Omega)$ where necessary, and summing over the appropriate nuclei.

We shall now specifically consider the scattering from methane. Methane is a spherical-top molecule with carbon at the center of mass, and the four C-H bonds arranged tetrahedrally (see Fig. 2). The permutation group of the protons is isomorphous with the point group T_d of the molecule. We shall assume, with Griffing, that the molecule is not excited from its ground vibrational state either thermally or by the neutron. This means we can confine our attention to the two lowest vibrational states, transforming according to the one-dimensional irreducible representations A_1 and A_2 and corresponding to even and odd parity, respectively. These two states will be effectively degenerate owing to the extremely high barrier for the inversion tunneling of the protons. Since A_1 and A_2 occur only once each, the summation over S in Eq. (15) disappears and because of the effective degeneracy of the two levels, the Boltzmann factor reduces to

$$P_J(T)=\frac{\exp(-E_J/k_BT)}{\sum_J n_J\exp(-E_J/k_BT)}, \tag{16}$$

where E_J is the energy of the rotational level J and n_J is the Wilson factor (see Table I) for that level (including both + and − parity states). The various matrix elements in Eq. (14) may now be evaluated. For the translational part we have

$$\langle\psi_t|\exp[i\mathbf{Q}\cdot\boldsymbol{\varrho}(t)]\exp[-i\mathbf{Q}\cdot\boldsymbol{\varrho}(0)]|\psi_t\rangle_T=\exp\{-(Q^2/2\mathfrak{M})(i\hbar t+t^2k_BT)\}, \tag{17}$$

as shown by Zemach and Glauber.[15] $\mathfrak{M}$ denotes the mass of the molecule. Further it is shown in Appendix B that

$$\begin{aligned}\langle\psi_K{}^{JM}\psi^{A_1}|\textstyle\sum_{\nu\mu}A_\nu A_\mu\exp[i\mathbf{Q}\cdot(\mathbf{b}_\nu(t)+\mathbf{u}_\nu(t))]\exp[-i\mathbf{Q}\cdot(\mathbf{b}_\mu(0)+\mathbf{u}_\mu(0))]|\psi^{A_1}\psi_{K'}{}^{JM}\rangle\\ =\langle\psi_K{}^{JM}\psi^{A_2}|\textstyle\sum_{\nu\mu}A_\nu A_\mu\exp[i\mathbf{Q}\cdot(\mathbf{b}_\nu(t)+\mathbf{u}_\nu(t))]\exp[-i\mathbf{Q}\cdot(\mathbf{b}_\mu(0)+\mathbf{u}_\mu(0))]|\psi^{A_2}\psi_{K'}{}^{JM}\rangle\\ =\textstyle\sum_{\nu\mu}A_\nu A_\mu\exp(-Q^2\gamma_{\nu\mu})\langle\psi_K{}^{JM}|\exp[i\mathbf{Q}\cdot\mathbf{b}_\nu(t)]\exp[-i\mathbf{Q}\cdot\mathbf{b}_\mu(0))]|\psi_{K'}{}^{JM}\rangle,\end{aligned} \tag{18}$$

where ψ^{A_1} and ψ^{A_2} stand for the vibrational parts of the wave function in the states A_1 and A_2. The quantity $\exp(-Q^2\gamma_{\nu\mu})$ on the right-hand side of Eq. (18) is the Debye-Waller factor associated with zero-point vibrations, the constant $\gamma_{\nu\mu}$ having the same meaning as in the work of Griffing. The rotational part, when evaluated using the methods of Rahman[6] and Yip[9] and summed over M, yields the result

$$\sum_M \langle \psi_K{}^{JM} | \exp[i\mathbf{Q}\cdot\mathbf{b}_\nu(t)] \exp[-i\mathbf{Q}\cdot\mathbf{b}_\mu(0)] | \psi_{K'}{}^{JM} \rangle = \sum_{J''K''} \exp[it(E_J - E_{J''})/\hbar](2J+1)(2J''+1)(-1)^{K+K'}$$
$$\sum_l (4\pi/(2l+1)) j_l(Qb_\nu) j_l(Qb_\mu) C(JJ''l;\, -KK'') C(JJ''l;\, -K'K'') Y_l{}^{(K-K'')}(\theta_\nu,\phi_\nu) Y_l{}^{(K'-K'')*}(\theta_\mu,\phi_\mu). \quad (19)$$

In deriving (19) we have expanded the matrix element in terms of the ordinary rotational final states $\psi_{K''}{}^{J''M''}$ rather than the symmetrized states. Since $\psi_{K''}{}^{J''M''}$ form a complete set, this is permissible. The C's are the usual Clebsch-Gordan coefficients,[19] the Y's are the spherical harmonics,[19] and j_l denotes the spherical Bessel function of order l. The (θ_ν,ϕ_ν) represent the polar co-ordinates of the νth nucleus with respect to a set of axes fixed in the molecule.[20]

Using Eqs. (14)–(19) in Eq. (2), and performing the time integration, we obtain for the coherent scattering cross section per molecule

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{\text{coh}} = \frac{1}{2\pi\hbar}\frac{k}{k_0}\left(\frac{2\pi\mathfrak{M}}{Q^2k_BT}\right)^{1/2} \sum_{JJ''} P_J(T) \exp\left\{-\frac{(\hbar\omega+\alpha)^2}{(2\hbar^2Q^2k_BT/\mathfrak{M})}\right\}$$
$$\times \sum_{KK'} L_{K'K} \sum_{\nu\mu} A_\nu A_\mu \exp(-Q^2\gamma_{\nu\mu}) F_{\nu\mu}(JJ''KK'), \quad (20)$$

where

$$\alpha = (\hbar^2Q^2/2\mathfrak{M}) - E_J + E_{J''}, \quad (21)$$

$$L_{K'K} = \sum_R (1/H)\{D_{K'K}{}^J(\bar{R}) \sum_\lambda \chi^{*(\lambda)}(R) \sum_\Omega n_\Lambda(\Omega) \sum_{V=A_1,A_2} \chi^{(V)}(R)\}, \quad (22)$$

and

$$F_{\nu\mu}(JJ''KK') = \sum_{K''} (2J+1)(2J''+1)(-1)^{K+K'} \sum_l (4\pi/(2l+1)) j_l(Qb_\nu) j_l(Qb_\mu)$$
$$\times C(JJ''l;\, -KK'') C(JJ''l;\, -K'K'') Y_l{}^{(K-K'')}(\theta_\nu,\phi_\nu) Y_l{}^{(K'-K'')*}(\theta_\mu,\phi_\mu). \quad (23)$$

It is to be noted that in Eq. (22) as R runs over the operations of T, $\bar{R}$ runs over the operations of the isomorphous group of pure rotations, O.

Remembering that carbon has zero incoherent-scattering amplitude, we have in a similar fashion for the incoherent scattering[21]

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{\text{inc}} = \frac{1}{2\pi\hbar}\frac{k}{k_0}\left(\frac{2\pi\mathfrak{M}}{Q^2k_BT}\right)^{1/2} \sum_{JJ''} P_J(T) \exp\left\{-\frac{(\hbar\omega+\alpha)^2}{(2\hbar^2Q^2k_BT/\mathfrak{M})}\right\}$$
$$\times\{\sum_{K'K} L_{K'K} \sum_p C_p{}^2 \exp(-Q^2\gamma_{pp}) F_{pp}(JJ''KK') + \sum_{K'K} M_{K'K} \sum_{\substack{p,p' \\ p\neq p'}} C_p{}^2 \exp(-Q^2\gamma_{pp'}) F_{pp'}(JJ''KK')\}, \quad (24)$$

where $L_{K'K}$ is as defined before and $M_{K'K}$ is given by

$$M_{K'K} = \sum_R (1/H)\{D_{K'K}{}^J(\bar{R}) \sum_\lambda \chi^{*(\lambda)}(R) \sum_\Omega Z(\Omega) n_\Lambda(\Omega) \sum_{V=A_1,A_2} \chi^{(V)}(R)\}. \quad (25)$$

The two terms on the right-hand side in Eq. (24) denote, respectively, the *self* and *interference* parts of the scattering. The terms may be regrouped in a slightly different fashion as

$$\{\sum_{K'K} M_{K'K} \sum_{pp'} C_p{}^2 \exp(-Q^2\gamma_{pp'}) F_{pp'}(JJ''KK') + \sum_{K'K} (L_{K'K} - M_{K'K}) \sum_p C_p{}^2 \exp(-Q^2\gamma_{pp}) F_{pp}(JJ''KK')\}, \quad (26)$$

to display respectively the *nonflip* and *flip* components of the incoherent cross section, as discussed previously. It is to be noted that $\chi^{A_1}(R) = -\chi^{A_2}(R)$ for operations of the group involving improper rotations, while $\chi^{A_1}(R) = +\chi^{A_2}(R)$ for operations involving pure rotations. Hence in the formulas given above, we could drop the summation over V and let R run over just the operations of the rotational subgroup T of T_d, and take H to be the order of this sub-

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[20] It is important to note that the operations R of the group must also be expressed with respect to the same set of axes.

[21] In writing out the terms explicitly, we shall denote ν and μ by p when they refer to the same proton, by p and p' when they refer to different protons, and by C when either of them refers to carbon.

TABLE II. Eulerian angles for the operations of the point group T. The operations are indicated by the permutations they effect on the protons (see Fig. 2). The Eulerian angles are defined as in Ref. 19. $\cos\theta = -(1/3)$.

Operation	α	β	γ
(1 2 3 4)	0	0	0
(1 4 2 3)	$(2/3)\pi$	0	0
(1 3 4 2)	$-(2/3)\pi$	0	0
(3 2 4 1)	$(4/3)\pi$	θ	$(1/3)\pi$
(4 2 1 3)	$(2/3)\pi$	θ	$(5/3)\pi$
(4 1 3 2)	0	θ	$(5/3)\pi$
(2 4 3 1)	$(4/3)\pi$	θ	π
(2 3 1 4)	$(2/3)\pi$	θ	π
(3 1 2 4)	0	θ	$(1/3)\pi$
(2 1 4 3)	0	θ	π
(4 3 2 1)	$(4/3)\pi$	θ	$(5/3)\pi$
(3 4 1 2)	$(2/3)\pi$	θ	$(1/3)\pi$

group. This in fact has been done by us in the numerical calculations, and bears a close resemblance to the way in which Wilson[5] calculates the multiplicity factors by considering essentially only the subgroup T. Further simplifications are possible in the expressions given above for the cross section. It is shown in Appendix C that $L_{K'K}F_{\nu\nu}(JJ''KK')$ is the same for all equivalent nuclei (i.e., all protons), and that $L_{K'K}F_{\nu\mu}(JJ''KK')$ and $M_{K'K}F_{\nu\mu}(JJ''KK')$ are the same for all equivalent pairs (i.e., all pairs pp and Cp). Further, methane being a spherical top, it is allowable and convenient to choose the molecule-fixed axes with the origin on the carbon atom, the Z axis along one of the C-H bonds, and the XZ plane containing another C-H bond (see Fig. 2). (The Eulerian angles for the various operations of T for this choice of axes are given in Table II.) In this case we have

$$F_{pp}(JJ''KK') = (2J+1)(2J''+1)(-1)^{K+K'} \textstyle\sum_l j_l^2(Qb_p) C(JJ''l; -KK) C(JJ''l; -K'K) \delta_{K'K}\,, \tag{27}$$

$$F_{pp'}(JJ''KK') = (2J+1)(2J''+1)(-1)^{K+K'} \textstyle\sum_l j_l^2(Qb_p)(4\pi/(2l+1))^{1/2} \times C(JJ''l; -KK) C(JJ''l; -K'K) P_l^{(K'-K)}(\theta_{pp'})\,, \tag{28}$$

$$F_{\mathrm{C}p}(JJ''KK') = (2J+1) j_0(Qb_p) \delta_{K'K} \delta_{JJ''}\,, \tag{29}$$

$$F_{\mathrm{CC}}(JJ''KK') = (2J+1) \delta_{K'K} \delta_{JJ''}\,, \tag{30}$$

where $\theta_{pp'}$ denotes the angle between two C-H bonds, and $P_l^m(\theta)$ is the associated Legendre polynomial.[19] We thus finally obtain

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{\mathrm{coh}} = \frac{1}{2\pi\hbar} \frac{k}{k_0} \left(\frac{2\pi\mathfrak{M}}{Q^2 k_B T}\right)^{1/2} \sum_{JJ''} P_J(T) \exp\left\{-\frac{(\hbar\omega+\alpha)^2}{(2\hbar^2 Q^2 k_B T/\mathfrak{M})}\right\} \times \sum_{K'K} L_{K'K} \{4A_p^2 \exp(-Q^2\gamma_{pp}) F_{pp}(JJ''KK') + 12A_p^2 \exp(-Q^2\gamma_{pp'}) F_{pp'}(JJ''KK') + 8A_{\mathrm{C}}A_p \exp(-Q^2\gamma_{\mathrm{C}p}) F_{\mathrm{C}p}(JJ''KK') + A_{\mathrm{C}}^2 \exp(-Q^2\gamma_{\mathrm{CC}}) F_{\mathrm{CC}}(JJ''KK')\}\,, \tag{31}$$

and

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{\mathrm{inc}} = \frac{1}{2\pi\hbar} \frac{k}{k_0} \left(\frac{2\pi\mathfrak{M}}{Q^2 k_B T}\right)^{1/2} \sum_{JJ''} P_J(T) \exp\left\{-\frac{(\hbar\omega+\alpha)^2}{(2\hbar^2 Q^2 k_B T/\mathfrak{M})}\right\} \times \{\sum_{K'K} L_{K'K} 4C_p^2 \exp(-Q^2\gamma_{pp}) F_{pp}(JJ''KK') + \sum_{K'K} M_{K'K} 12C_p^2 \exp(-Q^2\gamma_{pp'}) F_{pp'}(JJ''KK')\}\,, \tag{32}$$

with $F_{pp}(JJ''KK')$ etc., being given by Eqs. (27)–(30). It is interesting to compare the formulas in Eq. (31) and Eq. (32) with the expressions for the uncorrelated case,

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{\mathrm{coh}} = \frac{1}{2\pi\hbar} \frac{k}{k_0} \left(\frac{2\pi\mathfrak{M}}{Q^2 k_B T}\right)^{1/2} \sum_{JJ''} P_J(T) \exp\left\{-\frac{(\hbar\omega+\alpha)^2}{(2\hbar^2 Q^2 k_B T/\mathfrak{M})}\right\} \times (2J+1)(2J''+1) \{4A_p^2 \exp(-Q^2\gamma_{pp}) \sum_{l=|J-J''|}^{J+J''} j_l^2(Qb_p) + 12A_p^2 \exp(-Q^2\gamma_{pp'}) \times \sum_{l=|J-J''|}^{J+J''} j_l^2(Qb_p) P_l(\theta_{pp'}) + 8A_{\mathrm{C}}A_p \exp(-Q^2\gamma_{\mathrm{C}p}) j_0(Qb_p) \delta_{JJ''} + A_{\mathrm{C}}^2 \exp(-Q^2\gamma_{\mathrm{CC}}) \delta_{JJ''}\}\,, \tag{33}$$

and

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{\mathrm{inc}} = \frac{1}{2\pi\hbar} \frac{k}{k_0} \left(\frac{2\pi\mathfrak{M}}{Q^2 k_B T}\right)^{1/2} \sum_{JJ''} P_J(T) \exp\left\{-\frac{(\hbar\omega+\alpha)^2}{(2\hbar^2 Q^2 k_B T/\mathfrak{M})}\right\} \times (2J+1)(2J''+1) \{4C_p^2 \exp(-Q^2\gamma_{pp}) \sum_{l=|J-J''|}^{J+J''} j_l^2(Qb_p)\} \tag{34}$$

derived by Griffing. In the last two equations, $P_J(T)$ has the meaning

$$P_J(T)=\frac{\exp(-E_J/k_BT)}{\sum_J(2J+1)^2\exp(-E_J/k_BT)} \tag{35}$$

and $P_l(\theta)$ is the Legendre polyonmial. We observe that apart from the difference in $P_J(T)$ due to the Wilson factor there are several other differences in the expression for the two cases, and the complexity of the formulas for the correlated case arises essentially from the mixing of the states with different K.

B. Symmetric-Top Molecule

The discussion given above for the spherical-top molecule is easily extended to symmetric-top molecules like ammonia. In this case, part of the $(2J+1)$-fold K degeneracy is removed, and only the levels with $K=\pm|K|$ for a given J are degenerate. The rotational levels may thus be labeled by $(J,|K|)$ and the reducible basis that we must start with is $\psi_t\psi_\beta{}^{VS}\psi_K{}^{JM}$, with β running over all rows of S as before, but K now restricted to $\pm|K|$. By constructing symmetrized functions from this unsymmetrized basis and proceeding exactly as before[22] we obtain instead of Eq. (20)

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{\text{coh}}=\frac{1}{2\pi\hbar}\frac{k}{k_0}\left(\frac{2\pi\mathfrak{M}}{Q^2k_BT}\right)^{1/2}\sum_J\sum_{|K|=0}^{J}P_{J|K|}(T)\sum_{J''}\sum_{|K''|=0}^{J''}\exp\left\{-\frac{(\hbar\omega+\alpha)^2}{(2\hbar^2Q^2k_BT/\mathfrak{M})}\right\}$$
$$\times\sum_{K=\pm|K|}\;\sum_{K'=\pm|K|}\;\sum_{\nu\mu}A_\nu A_\mu\exp(-Q^2\gamma_{\nu\mu})F_{\nu\mu}(JJ''KK'|K''|), \tag{36}$$

where

$$\alpha=\hbar^2Q^2/2\mathfrak{M}-E_{JK}+E_{J''K''},$$

and $L_{K'K}$ is the same as in Eq. (22); $F_{\nu\mu}(JJ''KK'|K''|)$ is also the same as in Eq. (23) but with the summation over K'' being restricted to $\pm|K''|$. The Boltzmann factor $P_{J|K|}(T)$ is now given by

$$P_{J|K|}(T)=\frac{\exp(-E_{J|K|}/k_BT)}{\sum_{J|K|}n_{J|K|}\exp(-E_{J|K|}/k_BT)},$$

$n_{J|K|}$ being the Wilson factor for the level $(J,|K|)$ including as before, both positive- and negative-parity states. Similarly for incoherent scattering we have

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{\text{inc}}=\frac{1}{2\pi\hbar}\frac{k}{k_0}\left(\frac{2\pi\mathfrak{M}}{Q^2k_BT}\right)^{1/2}\sum_J\sum_{|K|=0}^{J}P_{J|K|}(T)\sum_{J''}\sum_{|K''|=0}^{J''}\exp\left\{-\frac{(\hbar\omega+\alpha)^2}{(2\hbar^2Q^2k_BT/\mathfrak{M})}\right\}$$
$$\times\Big\{\sum_{K=\pm|K|}\;\sum_{K'=\pm|K|}L_{K'K}\sum_\nu C_\nu{}^2\exp(-Q^2\gamma_{\nu\nu})F_{\nu\nu}(JJ''KK'|K''|)$$
$$+\sum_{K=\pm|K|}\;\sum_{K'=\pm|K|}M_{K'K}\sum_{\substack{\nu\neq\mu,\\ \text{identical}\\ \text{nuclei}}}C_\nu{}^2\exp(-Q^2\gamma_{\nu\mu})F_{\nu\mu}(JJ''KK'|K''|)\Big\}, \tag{37}$$

$M_{K'K}$ having the same meanings as in Eq. (25). The corresponding expressions in the uncorrelated case are

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{\text{coh}}=\frac{1}{2\pi\hbar}\frac{k}{k_0}\left(\frac{2\pi\mathfrak{M}}{Q^2k_BT}\right)^{1/2}\sum_{JK}P_{J|K|}(T)\sum_{J''K''}\exp\left\{-\frac{(\hbar\omega+\alpha)^2}{(2\hbar^2Q^2k_BT/\mathfrak{M})}\right\}$$
$$\times\sum_{\nu\mu}A_\nu A_\mu\exp(-Q^2\gamma_{\nu\mu})(2J+1)(2J''+1)\sum_l\frac{4\pi}{2l+1}j_l(Qb_\nu)j_l(Qb_\mu)$$
$$\times Y_l{}^{(K-K'')}(\theta_\nu,\phi_\nu)Y_l{}^{(K-K'')*}(\theta_\mu,\phi_\mu)[C(JJ''l;\,-KK'')]^2, \tag{38}$$

and

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{\text{inc}}=\frac{1}{2\pi\hbar}\frac{k}{k_0}\left(\frac{2\pi\mathfrak{M}}{Q^2k_BT}\right)^{1/2}\sum_{JK}P_{J|K|}(T)\sum_{J''K''}\exp\left\{-\frac{(\hbar\omega+\alpha)^2}{(2\hbar^2Q^2k_BT/\mathfrak{M})}\right\}$$
$$\times\sum_\nu C_\nu{}^2\exp(-Q^2\gamma_{\nu\nu})(2J+1)(2J''+1)\sum_l\frac{4\pi}{2l+1}j_l{}^2(Qb_\nu)|Y_l{}^{(K-K'')}(\theta_\nu,\phi_\nu)|^2[C(JJ''l;\,-KK'')]^2, \tag{39}$$

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[22] As in the case of the spherical-top molecule, the inversion splitting in the symmetric-top molecules also is very small, at least for our purposes. The positive- and negative-parity levels are therefore effectively degenerate and this fact has been made use of in deriving Eqs. (36) and (37).

with

$$P_{J|K|}=\frac{\exp(-E_{J|K|}/k_BT)}{\sum_{JK}(2J+1)\exp(-E_{J|K|}/k_BT)}.$$

III. NUMERICAL RESULTS AND DISCUSSION

The expressions for the scattering by methane have been programmed for computation in a CDC-3600 computer and numerical calculations performed for several cases. The first case studied was the same as that considered by Michael, i.e., the scattering of 0.025-eV neutrons through a 10° scattering angle by methane gas at 10°K. In the calculations, rotational states with J and $J''\leqslant 4$ were included. The results of the calculations are shown as a solid line in Fig. 3. The results were confirmed by an independent calculation in which the X, Y and Z axes were chosen along the three twofold axes of the molecule, respectively. The computing time for the latter choice of axes was nearly twice as long as that required for the choice indicated in Fig. 2, so that all the remaining cases were done with the axes as in Fig. 2. The dashed line in Fig. 3 shows the energy spectrum obtained in the uncorrelated case using the expressions in Eqs. (33) and (34). The results for the uncorrelated case have also been obtained in a different way by setting $M_{K'K}=0$ and $L_{K'K}=D_{K'K}{}^J(E)=\delta_{K'K}$, where E is the identity operation and $P_J(T)$ is given by Eq. (35). The two sets of results for the uncorrelated case agreed exactly with each other, as may be expected from a comparison of Eqs. (31) and (32) with Eqs. (33) and (34).

It is clear from Fig. 3 that spin-correlation produces appreciable differences in the scattering. The "elastic" scattering is enhanced by about 30%, the height of the peak representing the $0\rightarrow1$ transition is approximately doubled, and the $1\rightarrow2$ peak is lowered appreciably. This is in contrast to very small difference which Michael obtained in his calculations.

Note added in proof. The numerical results for the correlated case at 10°K presented earlier[14] are in error. The correct results are shown in Fig. 3.

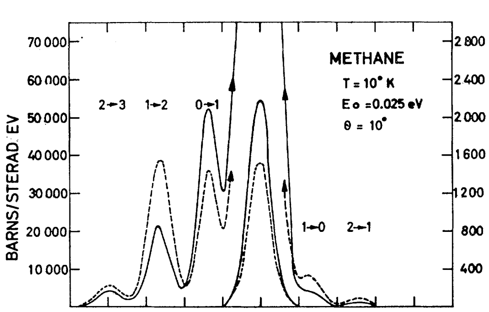

FIG. 3. Results for the scattering of neutrons by methane gas at 10°K. The solid line refers to the correlated case and the broken line to the uncorrelated case. The transitions associated with the various rotational peaks are also indicated.

Figure 4 shows the different contributions to the scattering. It may be seen that nonflip transitions are appreciable only in the "elastic" region. This is to be expected since there are very few symmetry-conserving transitions possible between states of different J among the first few rotational levels. (See Fig. 1.) It may also be noted that the interference term (pp') in the incoherent scattering, which identically vanished in the absence of spin correlations, is appreciable in both the "elastic" and "inelastic" regions, whereas the self term (pp) is diminished relative to the uncorrelated case.

The calculations were repeated for the case of 300°K taking into account rotational levels with J, $J''\leqslant 9$. The results are shown in Fig. 5. Similar calculations performed for the uncorrelated case yielded almost exactly the same results, the difference being at the most 0.7%.

We may thus conclude that spin correlations play an important role in determining the scattering at low temperatures, but their effect is very much reduced at higher temperatures, as anticipated by Zemach and Glauber.

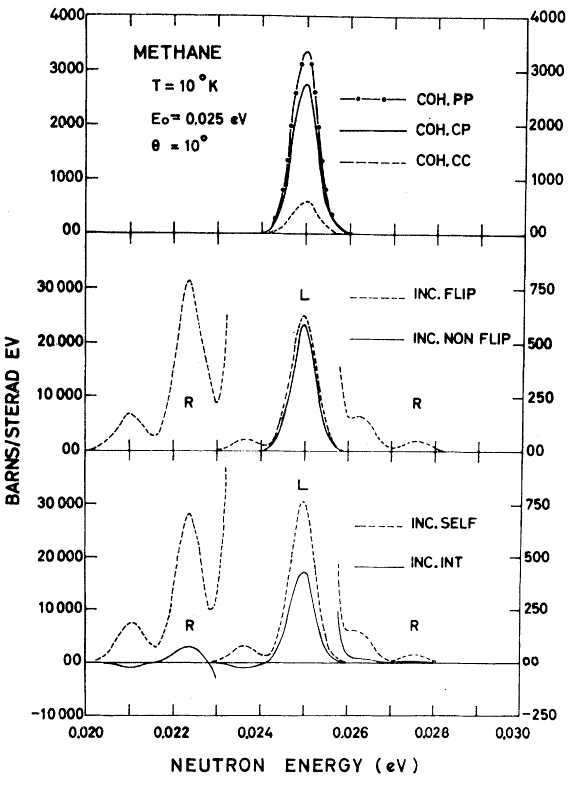

FIG. 4. The various contributions to the scattering at 10°K in the correlated case. L and R denote, respectively, the scales on the left-hand side and the right-hand side of the figure.

A possible further application of the formulation developed here is to the case of hindered rotations. If we consider the "weak-field" limit where the molecules are only slightly hindered by a fluctuating field which has no symmetry, then the degenerate manifold of rotational states characterized by (J,M) will be split into a number of levels corresponding to the irreducible representations of the point group of the molecule, as this symmetry will still be left in the Hamiltonian. Then the "symmetrized" wave functions discussed above may be regarded as good "zero-order" wave functions to be used to calculate the scattering. Additional complications would of course be introduced by the fact that the final states would now also have to be expressed as symmetrized combinations.

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APPENDIX A

We shall prove the relation (11) given in the text. Consider the matrix $\mathbf{A}$ which completely reduces the representation of $\mathcal{P}$ provided by the basis ψ_j. Let us denote the symmetrized function $\phi(\lambda\alpha r)$ with the help of a single suffix i as ϕ_i, with i running over all the rows of all the irreducible representations contained in the reducible representation generated from the basis ψ_j. We then have

$$\phi_i=\sum_j A_{ji}\psi_j. \tag{A1}$$

Now if O is any operator, we can, using our compact suffix, write

$$\sum_{r\alpha}\langle\phi(\lambda\alpha r)|O|\phi(\lambda\alpha r)\rangle=\sum_i{}^{\lambda}\langle\phi_i|O|\phi_i\rangle, \tag{A2}$$

where the superscript on the summation on the right-hand side denotes that it picks out only rows transforming according to the irreducible representation λ. Using Eq. (A1), we then obtain

$$\begin{aligned}\sum_{r\alpha}&\langle\phi(\lambda\alpha r)|O|\phi(\lambda\alpha r)\rangle\\ &=\sum_i{}^{\lambda}\{\sum_{jj'} A_{ji}{}^*A_{j'i}\langle\psi_j|O|\psi_{j'}\rangle\}\\ &=\sum_{jj'}\{\sum_i{}^{\lambda} A_{j'i}A_{ij}{}^{-1}\}\langle\psi_j|O|\psi_{j'}\rangle.\end{aligned} \tag{A3}$$

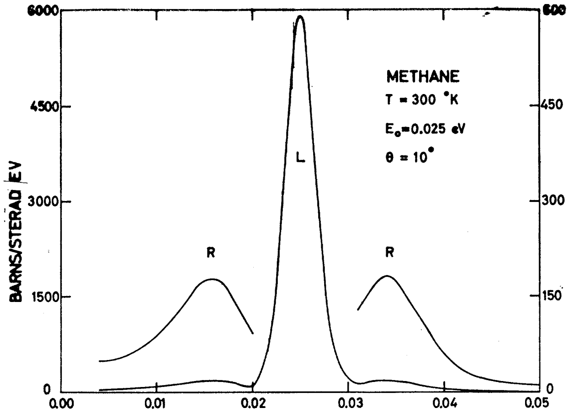

FIG. 5. Results for the scattering of neutrons by methane gas at 300°K in the correlated case. As in the previous figure, L and R denote the scales on the left and right side, respectively. The uncorrelated case gives almost the same results, the difference being at the most 0.7%.

We have used the unitary property of $\mathbf{A}$ in deriving the last step. Consider now the matrix $\mathbf{U}$ defined by

$$\mathbf{U}=\sum_{R\in\mathcal{P}}\mathbf{A}^{-1}\mathbf{R}\mathbf{A}\chi^{*(\lambda)}(R), \tag{A4}$$

where $\mathbf{R}$ denotes the reducible representation of the operator R of the group with respect to the basis ψ_j. Since $\mathbf{A}$ completely reduces the representation $\mathbf{R}$, the matrix $\mathbf{A}^{-1}\mathbf{R}\mathbf{A}$ will have the box diagonal form

$$\mathbf{A}^{-1}\mathbf{R}\mathbf{A}=\begin{bmatrix}D^{(1)}(R) & & & \\ & D^{(2)}(R) & & \\ & & \ddots & \\ & & & D^{(S)}(R)\end{bmatrix},$$

where $D^{(1)}(R)$, $D^{(2)}(R)$, $\cdots D^{(S)}(R)$ denote the S different irreducible representations (not necessarily all distinct) contained in $\mathbf{R}$. It is clear that $\mathbf{U}$ also will have a box diagonal form. A typical element of $\mathbf{U}$ will be

$$U_{\alpha\beta}=\sum_R (A^{-1}RA)_{\alpha\beta}\sum_k D_{kk}{}^{*(\lambda)}(R), \tag{A5}$$

where k runs over all the rows of the irreducible representation λ.

We now recall a well-known theorem regarding irreducible representations[18] which states that

$$\sum_R D_{ij}{}^{(\mu)}(R)D_{kl}{}^{*(\lambda)}(R)=(H/m_\lambda)\delta_{\mu\lambda}\delta_{ik}\delta_{jl}. \tag{A6}$$

Making use of this orthogonality relation, it is easily seen that

$$\begin{aligned}U_{\alpha\beta}&=(H/m_\lambda)\delta_{\alpha\beta} \text{ if } \alpha \text{ and } \beta \text{ refer to diagonal boxes corresponding to the species } \lambda,\\ &=0 \qquad \text{otherwise.}\end{aligned} \tag{A7}$$

In other words, $\mathbf{U}$ is a diagonal matrix with (H/m_λ) along rows which transform according to λ, and with zero in other rows.

Let us now define another matrix **P** by

$$\mathbf{P}=\sum\nolimits_R \chi^{*(\lambda)}(R)\mathbf{R}. \tag{A8}$$

From Eq. (A4) we have

$$\mathbf{P}=\mathbf{AUA}^{-1}. \tag{A9}$$

Thus

$$P_{j'j}=\sum_{l'l}A_{j'l'}U_{l'l}A_{lj}^{-1}=(H/m_\lambda)\sum_i{}^{\lambda} A_{ji}A_{ij}^{-1}. \tag{A10}$$

But, from (A8)

$$P_{j'j}=\sum\nolimits_R \chi^{*(\lambda)}(R)R_{j'j}, \tag{A11}$$

whence Eq. (A3) becomes

$$\sum_{r,\alpha}\langle\phi(\lambda\alpha r)|O|\phi(\lambda\alpha r)\rangle =\sum_{jj'}(m_\lambda/H)\chi^{*(\lambda)}(R)R_{j'j}\langle\psi_j|O|\psi_{j'}\rangle, \tag{A12}$$

which is the required result.

APPENDIX B

In this appendix, we shall establish the relation given in Eq. (18). Let g denote collectively all the vibrational coordinates $\mathbf{u}_\nu$ associated with a given configuration of the methane molecule, where $\mathbf{u}_\nu$ is given by [see Eq. (14)]

$$\mathbf{u}_\nu=\mathbf{r}_\nu-\boldsymbol{\varrho}-\mathbf{b}_\nu. \tag{B1}$$

Further, let $\bar{g}$ stand for the coordinates $\bar{\mathbf{u}}_\nu$ associated with the "inverted" configuration. $\bar{\mathbf{u}}_\nu$ is given by

$$\bar{\mathbf{u}}_\nu=\mathbf{r}_\nu-\boldsymbol{\varrho}+\mathbf{b}_\nu. \tag{B2}$$

If $\psi_{\mathrm{v}}(g)$ describes the ground-state vibrational wave function, then because of the inversion symmetry of the molecular Hamiltonian, $\psi_{\mathrm{v}}(\bar{g})$ must also be a wave function with the same eigenvalue. However, neither $\psi_{\mathrm{v}}(g)$ nor $\psi_{\mathrm{v}}(\bar{g})$ has a well-defined parity, and since the wave functions must have a well-defined parity, we construct the linear combinations

$$(1/\sqrt{2})\{\psi_v(g)+\psi_v(\bar{g})\}, \tag{B3}$$

$$(1/\sqrt{2})\{\psi_v(g)-\psi_v(\bar{g})\} \tag{B4}$$

having, respectively, positive and negative parities. Evidently (B3) transforms according to the irreducible representation A_1 [since $\psi_v(g)$ and $\psi_v(\bar{g})$ both transform according to A_1, being ground-state wave functions], while (B4) transforms according to A_2; and we may denote them simply as ψ^{A_1} and ψ^{A_2}. The two states ψ^{A_1} and ψ^{A_2} are effectively degenerate owing to the high barrier for inversion tunneling. Physically this would mean that the nuclei are strongly localized about their equilibrium positions and that $\psi_v(g)$ and $\psi_v(\bar{g})$ overlap very little. We may therefore write

$$\begin{aligned}\langle\psi_K{}^{JM}\psi^{A_1}|\sum_{\nu\mu} A_\nu A_\mu \exp[i\mathbf{Q}\cdot(\mathbf{u}_\nu(t)+\mathbf{b}_\nu(t))]\exp[-i\mathbf{Q}\cdot(\mathbf{u}_\mu(0)+\mathbf{b}_\mu(0))]|\psi^{A_1}\psi_{K'}{}^{JM}\rangle\\ =\sum_{\nu\mu} A_\nu A_\mu\langle\psi_K{}^{JM}|\exp[i\mathbf{Q}\cdot\mathbf{b}_\nu(t)]\exp[-i\mathbf{Q}\cdot\mathbf{b}_\mu(0)]|\psi_{K'}{}^{JM}\rangle\langle\psi^{A_1}|\exp[i\mathbf{Q}\cdot\mathbf{u}_\nu(t)]\exp[-i\mathbf{Q}\cdot\mathbf{u}_\mu(0)]|\psi^{A_1}\rangle_{\mathrm{av}}\\ =\sum_{\nu\mu}\tfrac{1}{2}A_\nu A_\mu\{\langle\psi_v(g)|V_{\nu\mu}|\psi_v(g)\rangle_{\mathrm{av}}+\langle\psi_v(\bar{g})|V_{\nu\mu}|\psi_v(\bar{g})\rangle_{\mathrm{av}}\}G_{\nu\mu}.\end{aligned} \tag{B5}$$

The suffix av above denotes an average over orientations. It is necessary when the rotational and vibrational parts are separated, as explained in Sec. II. The operator $V_{\nu\mu}$ is $\exp[i\mathbf{Q}\cdot\mathbf{u}_\nu(t)]\exp[-i\mathbf{Q}\cdot\mathbf{u}_\mu(0)]$, and $G_{\nu\mu}$ is the rotational matrix element. In a similar fashion, we can show that the right-hand side of (B5) is also equal to

$$\langle\psi_K{}^{JM}\psi^{A_2}|\sum_{\nu\mu} A_\nu A_\mu \exp[i\mathbf{Q}\cdot(\mathbf{u}_\nu(t)+\mathbf{b}_\nu(t))] \times\exp[-i\mathbf{Q}\cdot(\mathbf{u}_\mu(0)+\mathbf{b}_\mu(0))]|\psi^{A_2}\psi_{K'}{}^{JM}\rangle.$$

Now let us consider

$$\langle\psi_K{}^{JM}\psi^{A_1}|\sum_{\nu\mu} A_\nu A_\mu \exp[i\mathbf{Q}\cdot(\mathbf{u}_\nu(t)+\mathbf{b}_\nu(t))] \times\exp[-i\mathbf{Q}\cdot(\mathbf{u}_\mu(0)+\mathbf{b}_\mu(0))]|\psi^{A_2}\psi_{K'}{}^{JM}\rangle.$$

This can be expressed in the form

$$\langle\psi^{A_1}|\sum_{\nu\mu} A_\nu A_\mu G_{\nu\mu}V_{\nu\mu}|\psi^{A_2}\rangle_{\mathrm{av}}. \tag{B6}$$

Since the operator inside the matrix element in (B6) is invariant under the group of permutations of identical nuclei, the matrix element vanishes.[18] On the other hand, substituting for ψ^{A_1} and ψ^{A_2} from Eqs. (B3) and (B4), we obtain [neglecting overlap integrals between $\psi_v(g)$ and $\psi_v(\bar{g})$],

$$\langle\psi^{A_1}|\sum_{\nu\mu} A_\nu A_\mu G_{\nu\mu}V_{\nu\mu}|\psi^{A_2}\rangle_{\mathrm{av}} =\sum_{\nu\mu}\tfrac{1}{2}A_\nu A_\mu G_{\nu\mu}\{\langle\psi_v(g)|V_{\nu\mu}|\psi_v(g)\rangle_{\mathrm{av}} -\langle\psi_v(\bar{g})|V_{\nu\mu}|\psi_v(\bar{g})\rangle_{\mathrm{av}}\}.$$

Hence

$$\langle\psi_v(g)|V_{\nu\mu}|\psi_v(g)\rangle_{\mathrm{av}}=\langle\psi_v(\bar{g})|V_{\nu\mu}|\psi_v(\bar{g})\rangle_{\mathrm{av}}. \tag{B7}$$

The quantity $\langle\psi_v(g)|V_{\nu\mu}|\psi_v(g)\rangle$ has been evaluated by Griffing and shown to be equal to $\exp(-Q^2\gamma_{\nu\mu})$, where $\gamma_{\nu\mu}$ is a constant. Using this result and (B7) in (B5) we obtain the result quoted in Eq. (18).

APPENDIX C

Because of the symmetry of the molecule, every proton can be transformed into any other proton by a rotation S belonging to the point group O which, as we have already remarked, is isomorphous to the point group T_d. Likewise all proton-proton pairs can be transformed into each other by the operations of O, and the same is true of all carbon-proton pairs. Thus for each term in the sum over ν or (ν,μ) in

$$L_{K'K}\sum_{\nu\mu}A_\nu A_\mu\exp(-Q^2\gamma_{\nu\mu})F_{\nu\mu}(JJ''KK'),$$

and

$$M_{K'K}\sum_{\nu\mu}C_\nu{}^2\exp(-Q^2\gamma_{\nu\mu})F_{\nu\mu}(JJ''KK'),$$

or

$$(L_{K'K}-M_{K'K})\sum_\nu C_\nu{}^2\exp(-Q^2\gamma_{\nu\nu})F_{\nu\nu}(JJ''K'K),$$

which involve protons [see Eqs. (20) and (24) and (26)], we transform the molecular axes by the rotation S in order to keep the arguments (θ_ν, ϕ_ν) and (θ_μ,ϕ_μ) the same. Since $\bar{R}$ will now have to be expressed in terms of the new axes, we shall have to replace $D_{K'K}{}^J(\bar{R})$ by $D_{K'K}{}^J(S^{-1}\bar{R}S)$. Further since

$$\chi^{*(\lambda)}(R)=\chi^{*(\lambda)}(\bar{R})=\chi^{*(\lambda)}(S^{-1}\bar{R}S),$$

and in a similar fashion

$$\chi^{(V)}(R)=\chi^{(V)}(S^{-1}\bar{R}S),$$

we may write for each transformed term

$$L_{K'K}=\sum_{\bar{R}\in O}(1/H)\{\sum_\lambda\chi^{*(\lambda)}(S^{-1}\bar{R}S)\sum_\Omega n_\Lambda(\Omega)$$
$$\times\sum_{V=A_1,A_2}\chi^{(V)}(S^{-1}\bar{R}S)\}D_{K'K}{}^J(S^{-1}\bar{R}S).$$

Now $S^{-1}\bar{R}S$ is simply another member of the group O, and as we are summing over all the operations of the group, $L_{K'K}$ will be unchanged as a result of the transformation by S. It follows, therefore, that $L_{K'K}F_{\nu\nu}\times(JJ''KK')$ is the same for all equivalent nuclei, and the sum over all such nuclei is simply obtained by calculating it for one nucleus in the equivalent set and multiplying it by the number of nuclei in the set. The same holds for all equivalent pairs (ν,μ) in $L_{K'K}F_{\nu\mu}\times(JJ''KK')$ and $M_{K'K}F_{\nu\mu}(JJ''KK')$.