Rotationally Resolved Optical Rotation and Circular Dichroism Effects for Symmetric Top Molecules Induced by a Resonant Circularly Polarized Pumping Optical Field

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The rotationally resolved laser-induced optical activity including the laser-induced optical rotation (LIOR) and laser-induced circular dichroism (LICD) effects of an IR probing light pumped by a collinear intense resonant circularly polarized light dependent on the third-order susceptibility due to the pure electric dipole interaction for achiral symmetric top molecules in the gas phase is discussed theoretically. The laser-induced optical activity contains four distinct contributions named *A*, *B*, *C*, and *D* terms: the *B* term of the LIOR and LICD arising from the rotational wave function perturbed by the pumping light is deduced using the semiclassical perturbation theory, and the expressions for *A*, *C*, and *D* terms, respectively, due to the ac Stark effect, the Boltzmann statistical redistribution, and the alteration of occupation polability, are obtained from previous results [Zheng, R.-H.; Chen, D.-M.; Wei, W.-M.; He, T.-J.; Liu, F.-C. *J. Chem. Phys.* **2004**, *121*, 6835]. The microwave−IR double resonant spectrum is proposed to detect the LIOR and LICD effects. As an example, the LIOR and LICD for the HCF_3 molecules in the conditions of 298.15 K and 0.3 Torr when the IR probing light sweeps over the rotational−vibrational transition of the υ_5 and υ_1 modes and the right circularly polarized microwave pumping light with the intensity of 1 kW cm^{-2} at the resonant frequency 40.84 GHz are calculated on the basis of the B3LYP/6-311++G** computations. The theoretical results indicate that the *B* term can be of the same order of magnitude as the *A* and *D* terms, and the LIOR and LICD can be measurable in comparison to the rotationally resolved MVCD. The laser-induced optical activity may provide useful new information and form a basis for a different kind of optical activity spectroscopy.

1. Introduction

Optical activity has been an attractive subject for chemists, physicists, and biochemists for a long time.[1−8] Optically active molecules interact differently with left and right circularly polarized light. This manifests itself in such well-known phenomena as optical rotation, circular dichroism, and Rayleigh and Raman optical activity. Faraday observed a linear effect of a magnetic field on optical rotation in 1846. Magnetic−optical rotation was later shown to occur in all matter.[5a] Since then, efforts have been made to find a similar effect caused by an electric or optical field; i.e., linear and nonlinear electrooptical optical activity.[9−29] In 1980, Buckingham and Shatwell reported the differential scattering of circularly polarized light by gaseous methyl chloride linear on applying an electrostatic field from interference of electric and magnetic dipole scattering.[9] In 1998, Buckingham and Fisher predicted a linear effect of an electrostatic field on the intensity of sum- and difference-frequency generation in a chiral liquid arising from the electric dipole interaction[10] and observed this effect five years later.[11] In 1993 and 1997, intensity-dependent optical rotation by a solution of optically active molecules, which was predicted in 1968,[14] was experimentally observed.[12,13] Since 1994, Byers et al. have discovered that surface second harmonic generation (SHG) can be shown to display optical rotation effects depending on the handedness of chiral molecules at various interfaces.[15−19] In 1999, Hache et al. introduced a nonlinear circular dichroism for a liquid chiral molecule due to nonlocal effects such as magnetic dipolar and electric quadrupolar ones[20,21] and presented experimental evidence later.[22−24] Recently, self-rotation due to the interaction of an elliptically polarized light field with an isotropic medium has been rapidly developed,[25,26] which is essentially not a real optical activity but an optical Kerr effect arising from nonlinear electronic response.[27−30] Though so many electrooptical optical activities have been introduced and observed, there is no simple electric analogue of the Faraday effect due to the requirements of time and reversal and parity symmetry.[3] For example, the electrooptical activity for the isotropic optically inactive molecule arising from pure electric dipole transition is rarely reported. In this paper, a different kind of nonlinear optical activity including optical rotation and circular dichroism due to the third-order polarizability from the pure electric dipole interaction for achiral symmetric top molecules in the gas phase is presented and discussed theoretically.

In the 1990s, Keiderling and co-workers did a series of experiments on the rotationally resolved magnetic vibrational circular dichroism (MVCD) for linear molecules[31] and symmetric top molecules.[32] It is known[33−35] that, when the light beam has some degree of circular polarization, this optical field is equivalent to an effective magnetic field, and a Zeeman light-induced shift can occur due to the ac Stark effect. In our previous paper,[36,37] the magnetic field in the MVCD for a linear molecule is replaced by a resonant circularly polarized intense pumping

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optical field, and the corresponding laser-induced circular dichroism effect by this pumping light is expected to occur. Similarly, the laser-induced optical rotation (LIOR) and laser-induced circular dichroism (LICD) are also expected to occur when a resonant circularly polarized pumping optical field takes the place of the magnetic field in the MVCD for symmetric top molecules.

In section 2, on the basis of the results in ref 37, the *A*, *C*, and *D* terms of LIOR and LICD for symmetric top molecules due to the *M*-dependent ac Stark splittings and shifts, *M*-dependent Boltzmann statistical redistribution, and *M*-dependent occupation probability repopulation by the pumping light are respectively deduced. Also, the *B* term of LIOR and LICD arising from the rotational wave function of the symmetric top molecule perturbed by the pumping light is taken into account in this paper and obtained using the semiclassical perturbation theory. In section 3, the microwave−IR double resonant spectrum is proposed to detect the LIOR and LICD effect. As an example, the LIOR and LICD for the HCF_3 molecules in the gas phase at the temperature of 298.15 K and the pressure of 0.3 Torr with 5 cm^{-1} optical path are calculated when the IR probing optical field sweeps over the rotational−vibrational transition of the v_5 and v_1 vibration modes and the circularly polarized microwave pumping light at the frequency of 40.84 GHz resonant with the rotation transition and with the intensity of 1 kW/cm^2 based on the B3LYP/6-311++G** computation. The results indicate that the *B* term of the laser-induced optical activity can be on the same order of magnitude as the *A* and *D* terms, and the *C* term is 2 orders of magnitude smaller than they are. In comparison with the MVCD, the LIOR and LICD are measurable, and the magnitude of LICD with the pumping optical field $I = 0.1$ kW cm^{-2} is equal to that of MVCD with the magnetic field of 1 T.

2. Theory

The experimental arrangement for laser-induced optical rotation and laser-induced circular dichroism for symmetric top molecules is a weak IR probing beam with the frequency v_0 propagating collinearly with an intense resonant circularly polarized pumping optical field with the frequency v_1.[37] The LIOR and LICD depend on the third-order susceptibility that is treated by the effective linear susceptibility method.[37,38]

In this section, the relation between the optical rotation and circular dichroism and the antisymmetric polarizabilities is presented first. Second, the expressions of the antisymmetric polarizability for rotational sublevels of a symmetric top molecule induced by a resonant circularly polarized light are described. Third, the *A*, *B*, *C*, and *D* terms of LIOR for a given rotational sublevel is considered. And last, the LIOR and LICD for a given rotational level $|JK\rangle$ are obtained.

A plane-polarized light is equivalent to the sum of right and left circularly polarized light of equal amplitude, and it may be shown that the rotation ϕ of the plane of polarization and θ of an initially plane polarized light of circular frequency v_0 propagating with the path length *z* are respectively determined by the real part and imaginary part of the antisymmetric polarizability α'_{xy} [5]

$$\phi = \frac{2\pi v_0 z}{2c}(n_- - n_+) = \frac{2\pi^2 N_g v_0 z}{c}\,\mathrm{Re}\langle\alpha'_{xy}\rangle \tag{1}$$

$$\theta = \frac{2\pi v_0 z}{2c}(k_- - k_+) = \frac{2\pi^2 N_g v_0 z}{c}\,\mathrm{Im}\langle\alpha'_{xy}\rangle \tag{2}$$

where the antisymmetric polarizability α'_{xy} can be expressed as[1,2,5]

$$\alpha'_{xy} = \sum_n \left[\frac{1}{2h}\frac{\langle g|er_x|n\rangle\langle n|er_y|g\rangle}{(v_{gn} - v_0 - i\Gamma_{gn})} - \frac{1}{2h}\frac{\langle g|er_y|n\rangle\langle n|er_x|g\rangle}{(v_{gn} - v_0 - i\Gamma_{gn})}\right]\rho^{(0)}_{gg} + c.c. \tag{3}$$

N_g and $\rho^{(0)}_{gg}$ are the number density and the population of molecules in the state $|g\rangle$, respectively, $\hat{n} = n - ik$ is the complex refractive index, and *n* and *k* are the real refractive index and absorption coefficient, respectively.[5,39,40] The monochromic right (+) or left (−) circularly polarized wave propagating along the *z* axis with the frequency v is described by the electric-field vector[5]

$$\vec{E}_\pm = \frac{1}{\sqrt{2}}E^{(0)}\exp[-i2\pi v(t - \hat{n}_\pm z/c)](\vec{\imath} \mp i\vec{\jmath}) + c.c. \tag{4}$$

and the interaction Hamiltonian describing the interaction of circularly polarized light with matter is

$$H_\pm = -\frac{1}{\sqrt{2}}er_\pm E^{(0)}\exp[-i2\pi v(t - \hat{n}_\pm z/c)] + c.c. \tag{5}$$

where $er_\pm = (1/\sqrt{2})\,e(x \mp iy)$ is the dipole moment operator.

2.1. LIOR for a Given Rotational Sublevel $|JKM\rangle$. Because the deduction process of LICD is very similar to that of LIOR, in this subsection only the expressions of LIOR is deduced, and those of LICD is omitted for simplification. Here, the LIOR effect in this paper is concerned with three energy levels, the ground state $|g\rangle$ and the intermediate states $|n\rangle$ and $|m\rangle$: the circularly polarized optical field v_1 pumps the system from $|g\rangle$ to $|m\rangle$, and the probing IR beam at the frequency v_0 scans over the transition between $|g\rangle$ and $|n\rangle$. Assume that the wave functions of a symmetric top molecule can be written as the product of separable vibronic and symmetric top rotational wave functions

$$|g\rangle = |\tilde{g}v\rangle|JKM\rangle \quad |n\rangle = |\tilde{n}v_n\rangle|J'K'M'\rangle \quad |m\rangle = |\tilde{m}v_m\rangle|J''K''M''\rangle \tag{6}$$

where $\tilde{g}$ and $\tilde{n}$ (or $\tilde{m}$) stand for the initial and intermediate electronic states in eq 7, respectively. v, *J*, *K*, and *M* are the quantum numbers for the vibrational, total angular momentum, top axis component, and space-fixed *z*-axis component of angular momentum, respectively. The unprimed, primed, and double-primed indices of rotation quantum numbers correspond to the states $|g\rangle$, $|n\rangle$, and $|m\rangle$, respectively.

The antisymmetric rotational polarizabilities for a symmetric top molecule induced by a resonant circularly polarized optical field are presented in the Appendix. Here, the results are cited including the population (diagonal density matrix elements) $\rho^{(0)}_{gg}$. The imaginary and real parts of the antisymmetric polarizability at v_1 or v_0 are both *M*-dependent

$$\mathrm{Re}(\alpha^i_M)^{ant} = Mf_i\rho^{(0)}_{gg} \tag{7}$$

$$\mathrm{Im}(\alpha^i_M)^{ant} = Mg_i\rho^{(0)}_{gg} \tag{8}$$

where $i = m$ or n for the transition $|\tilde{g}v\rangle \rightarrow |\tilde{m}v_m\rangle$ at resonant frequency v_1 or $|\tilde{g}v\rangle \rightarrow |\tilde{n}v_n\rangle$ at v_0, respectively, and the frequency factors g_i and f_i are, respectively

$$f_i(J) = [(2J+3)C^R_{K+\Delta K}(JK)f_{iR,K+\Delta K} - C^Q_{K+\Delta K}(JK)f_{iQ,K+\Delta K} - (2J-1)C^P_{K+\Delta K}(JK)f_{iP,K+\Delta K}] \quad (9)$$

$$g_i(J) = [(2J+3)C^R_{K+\Delta K}(JK)g_{iR,K+\Delta K} - C^Q_{K+\Delta K}(JK)g_{iQ,K+\Delta K} - (2J-1)C^P_{K+\Delta K}(JK)g_{iP,K+\Delta K}] \quad (10)$$

where the detailed expressions for the coefficient factor $C_{K+\Delta K}(JK)$ and frequency factors $f_{i,K+\Delta K}$ and $g_{i,K+\Delta K}$ are in the Appendix. In the following discussion, $f_i = f_i(J)$ and $g_i = g_i(J)$ except where otherwise stated.

When a resonant circularly polarized pumping field υ_1 is applied, α'_{xy} in eq 3 becomes a function of the frequency υ_1, intensity I, and polarization of the pumping light. Just as pointed out in ref 37, analogous to the magnetic field in magnetic optical activity, the pumping optical field has four effects on the antisymmetric polarizability, and to the first order in the pumping light intensity, the antisymmetric polarizability should be split into four terms related to the above effects, respectively, and the corresponding laser-induced optical rotation for a given rotational sublevel $|JKM\rangle$ yields A, B, C, and D terms

$$\phi_{JKM} = \phi^0_{JKM} + \phi^A_{JKM} + \phi^B_{JKM} + \phi^C_{JKM} + \phi^D_{JKM} \quad (11)$$

Here, ϕ^0_{JKM} is the optical rotation of the probing light when the pumping optical field is not applied and determined by the M-dependent antisymmetric polarizability of the rotational sublevel $|JKM\rangle$. From eqs 1 and 2 and ref 37, the A, C, and D terms of LIOR for symmetric top molecules can be obtained in a similar way of deducing the laser-induced circular dichroism for linear molecules and are presented as follows.

The A term of LIOR is from the laser-induced splittings and shifts of the degenerate rotational sublevels $|JKM\rangle$

$$\phi^A_{JKM} = \frac{2\pi^2 N_{g\upsilon J} z}{c} M A_\phi \Delta\upsilon_\pm \quad (12)$$

where $\Delta\upsilon_\pm$ is the ac Stark effect of rotational sublevels $|JKM\rangle$ induced by the resonant right (+) or left (−) circularly polarized pumping light and can be expressed as[37]

$$\Delta\upsilon_\pm = \frac{(E^{(0)})^2}{2h}[\mathrm{Re}(\alpha^m_M)^{\mathrm{sym}} \mp \mathrm{Re}(\alpha^m_M)^{\mathrm{ant}}] \quad (13)$$

when $(E^{(0)})^2|(M_0)^{\tilde{m}\upsilon'}_{\tilde{g}\upsilon}|^2 \ll \tau_g\Gamma_m$, τ_g is the spontaneous and collision decay width for the ground rotation level, and Γ_m is the spontaneous decay width for the rotation level $|m\rangle$. The frequency factor A_ϕ in eq 12 is

$$A_\phi = \left[\frac{\upsilon_0 {\Delta_{nR}}^2 C^R_{K+\Delta K}(JK)}{4(J+1)^2(2J+1)h[{\Delta_{nR}}^2 + {\Gamma_n}^2]^2} - \frac{\upsilon_0 {\Delta_{nQ}}^2 C^Q_{K+\Delta K}(JK)}{8J^2(J+1)^2 h[{\Delta_{nQ}}^2 + {\Gamma_n}^2]^2} - \frac{C^P_{K+\Delta K}(JK)\upsilon_0 {\Delta_{nP}}^2}{4J^2(2J+1)h[{\Delta_{nP}}^2 + {\Gamma_n}^2]^2}\right] (M_{(-\Delta K)})^{\tilde{g}\upsilon}_{\tilde{n}\upsilon_n}(M_{\Delta K})^{\tilde{n}\upsilon_n}_{\tilde{g}\upsilon} \quad (14)$$

and $\Delta K = 0, \pm 1$.

The C term of LIOR is from the differences of the Boltzmann statistical distribution of molecules in the state $|JKM\rangle$ (the number density N_M) due to the ac Stark splitting. If it is assumed that $h\Delta\upsilon_\pm \ll kT$, the C term can be expressed as

$$\phi^C_{JKM} = \frac{2\pi^2 N_{\tilde{g}J\upsilon} z}{c}\frac{h\Delta\upsilon_\pm}{kT} M C_\phi \quad (15)$$

which is inversely proportional to the temperature. And the frequency factor C_ϕ is

$$C_\phi = \upsilon_0 f_n \quad (16)$$

The D term of LIOR is from changes of the occupation probability in the sublevel $|JKM\rangle$, ρ_M, due to the optical pumping

$$\phi^D_{JKM} = \frac{2\pi^2 N_{\tilde{g}J\upsilon} z}{c} M C_\phi \Delta\rho_\pm \quad (17)$$

where $\rho_M = \rho^{(0)}_{gg} + \Delta\rho_\pm$ and

$$\Delta\rho_\pm = -\frac{(E^{(0)})^2}{h\tau_g}[\mathrm{Im}(\alpha^m_M)^{\mathrm{sym}} \mp \mathrm{Im}(\alpha^m_M)^{\mathrm{ant}}] \quad (18)$$

In our previous studies,[37] the B term arising from the wave functions of the ground rotational sublevels perturbed by the pumping optical field was not considered. Here, the B term is taken into account using the semiclassical perturbation theory. The wave functions of the rotational sublevel $|g\rangle$ perturbed by the right (+) or left (−) circularly polarized pumping light resonant with the transition $|g\rangle \rightarrow |m\rangle$ can be written as[41]

$$|g\rangle_\pm = |g\rangle + \sum_{|m\rangle}\frac{1}{h}\frac{\langle m|H_\pm|g\rangle}{\upsilon_{gm} - \upsilon_1 - i\Gamma_m}|m\rangle \quad (19)$$

where the line width Γ_m is included to avoid divergence when the light frequency υ_1 approaches the transition frequency υ_{gm}. By substituting eq 19 into eq 3, only the four-wave mixing term is reserved; the antisymmetric polarizability α'_{xy} can be rewritten as

$$(\alpha'_{xy})_\pm = \sum_n\left[\frac{1}{2h}\frac{\langle g|er_x|n\rangle\langle n|er_y|g\rangle}{(\upsilon_{gn} - \upsilon_0 - i\Gamma_{gn})} - \frac{1}{2h}\frac{\langle g|er_y|n\rangle\langle n|er_x|g\rangle}{(\upsilon_{gn} - \upsilon_0 - i\Gamma_{gn})}\right] + \sum_{n,m}\frac{1}{2h}\frac{(\langle m|er_x|n\rangle\langle n|er_y|m\rangle - \langle m|er_y|n\rangle\langle n|er_x|m\rangle)\langle g|H_\mp|m\rangle\langle m|H_\pm|g\rangle}{(\upsilon_{gn} - \upsilon_0 - i\Gamma_n)(\upsilon_{gm} - \upsilon_1 + i\Gamma_m)(\upsilon_{gm} - \upsilon_1 - i\Gamma_m)} \quad (20)$$

where the second term is the polarizability of the probing light when the influence of the pumping light is considered. Using eqs 1 and 20 and the angular momentum theory,[42] the B term of LIOR for the sublevel $|JKM\rangle$ is also temperature-independent and can be written as two terms: one is M^2-dependent, and the other is M- and M^3-dependent.

$$\phi^B_{JKM} = \frac{2\pi^2 N_{g\upsilon J} z}{c}\frac{(E^{(0)})^2}{2h}M(MB_\phi + B'_\phi) \quad (21)$$

Here, the frequency factor B_ϕ is

$$B_\phi = (M_{(-\Delta K)})^{\tilde{n}\upsilon_n}_{\tilde{m}\upsilon_m}(M_{\Delta K})^{\tilde{m}\upsilon_m}_{\tilde{n}\upsilon_n}\left[\frac{\upsilon_0 C^R_{K+\Delta K}(J,K)f_n(J+1)}{4(J+1)^2(2J+1)h(\Delta_{mR,K+\Delta K}{}^2+\Gamma_m{}^2)} + \frac{\upsilon_0 C^Q_{K+\Delta K}(J,K)f_n(J)}{8J^2(J+1)^2h(\Delta_{mQ,K+\Delta K}{}^2+\Gamma_m{}^2)} + \frac{\upsilon_0 C^P_{K+\Delta K}(J,K)f_n(J-1)}{4J^2(2J-1)(2J+1)h(\Delta_{mP,K+\Delta K}{}^2+\Gamma_m{}^2)}\right] \quad (22)$$

It should be noted that the transition moments in eq 22 are not $(M_{(-\Delta K)})^{n\upsilon_n}_{g\upsilon}(M_{\Delta K})^{g\upsilon}_{n\upsilon_n}$ but $(M_{(-\Delta K)})^{n\upsilon_n}_{m\upsilon_m}(M_{\Delta K})^{m\upsilon_m}_{n\upsilon_n}$. Equation 22 shows that, different from the *A*, *C*, and *D* terms, the *B* term cannot be explicitly expressed into the product of the polarizabilities respectively induced by the probing and the pumping light. B'_ϕ in eq 21 contains both a constant and M^2-dependent frequency factors, and its expression is omitted for it provides no contribution to LIOR for a given rotational level $|JK\rangle$ when eq 21 is summed over *M* (see next subsection).

2.2. Rotationally Resolved LIOR and LICD. When the pumping optical field is not intense enough to separate the individual rotational sublevel $|JKM\rangle$ and the decay widths, and the line widths are large compared with the laser-induced shifts and splittings, we study LIOR and LICD for the given rotation level $|JK\rangle$. By summing ϕ_{JKM} over rotational sublevels $|JKM\rangle$, we obtain the LIOR for a given rotational level $|JK\rangle$

$$\phi_{JK} = \phi^A_{JK} + \phi^B_{JK} + \phi^C_{JK} + \phi^D_{JK}$$
$$= \sum_{M=-J}^{J}(\phi^A_{JKM}) + \sum_{M=-J}^{J}(\phi^B_{JKM}) + \sum_{M=-J}^{J}(\phi^C_{JKM}) + \sum_{M=-J}^{J}(\phi^D_{JKM}) \quad (23)$$

Note that $\sum_M \phi^0_{JKM}$ is zero and is neglected in eq 23. All of the *A*, *B*, *C*, and *D* terms in eq 33 can be expressed as two terms according to eqs 7−10, 12−18, and 21−22: one is M^2-dependent arising from the interaction of the antisymmetric polarizabilities respectively induced by the probing and pumping optical fields, which is nonzero in summing over *M*; the other term is *M*- and M^3-dependent from the interaction of the antisymmetric polarizability by the probing optical field and the symmetric polarizability by the pumping optical field, which is zero in summing over *M*. Thus, the *A*, *B*, *C*, and *D* terms of the laser-induced optical rotation for the rotation level $|JK\rangle$ are, respectively

$$\phi^A_{JK} = \mp\frac{J(J+1)(2J+1)}{3}\frac{I}{h\epsilon_0 c}\frac{2\pi^2 N_{\tilde{g}\upsilon J} z A_\phi f_m}{c} \quad (24)$$

$$\phi^B_{JK} = \mp\frac{J(J+1)(2J+1)}{3}\frac{I}{h\epsilon_0 c}\frac{2\pi^2 N_{\tilde{g}\upsilon J} z B_\phi}{c} \quad (25)$$

$$\phi^C_{JK} = \mp\frac{J(J+1)(2J+1)}{3}\frac{I}{h\epsilon_0 c}\frac{2\pi^2 h N_{\tilde{g}\upsilon J} z C_\phi f_m}{ckT} \quad (26)$$

$$\phi^D_{JK} = \pm\frac{J(J+1)(2J+1)}{3}\frac{I}{h\epsilon_0 c}\frac{2\pi^2 N_{\tilde{g}\upsilon J} z C_\phi g_m}{c\tau_M} \quad (27)$$

Similarly, the *A*, *B*, *C*, and *D* terms of the laser-induced circular dichroism (LICD) for the rotation level $|JK\rangle$ are, respectively

$$\theta^A_{JK} = \mp\frac{J(J+1)(2J+1)}{3}\frac{I}{h\epsilon_0 c}\frac{2\pi^2 N_{\tilde{g}\upsilon J} z A_\theta f_m}{c} \quad (28)$$

$$\theta^B_{JK} = \mp\frac{J(J+1)(2J+1)}{3}\frac{I}{h\epsilon_0 c}\frac{2\pi^2 N_{\tilde{g}\upsilon J} z B_\theta}{c} \quad (29)$$

$$\theta^C_{JK} = \mp\frac{J(J+1)(2J+1)}{3}\frac{I}{h\epsilon_0 c}\frac{2\pi^2 h N_{\tilde{g}\upsilon J} z C_\theta f_m}{ckT} \quad (30)$$

$$\theta^D_{JK} = \pm\frac{J(J+1)(2J+1)}{3}\frac{I}{h\epsilon_0 c}\frac{2\pi^2 N_{\tilde{g}\upsilon J} z C_\theta g_m}{c\tau_M} \quad (31)$$

Here, the frequency factor for the *A* term of LICD is

$$A_\theta = \left[\frac{\upsilon_0\Delta_{nR}\Gamma_n C^R_{K+\Delta K}(JK)}{4(J+1)^2(2J+1)h[\Delta_{nR}{}^2+\Gamma_n{}^2]^2} - \frac{\upsilon_0\Delta_{nQ}\Gamma_n C^Q_{K+\Delta K}(JK)}{8J^2(J+1)^2h[\Delta_{nQ}{}^2+\Gamma_n]^2} - \frac{\upsilon_0\Delta_{nP}\Gamma_n C^P_{K+\Delta K}(JK)}{4J^2(2J+1)h[\Delta_{nP}{}^2+\Gamma_n{}^2]^2}\right](M_{(-\Delta K)})^{\tilde{g}\upsilon}_{\tilde{n}\upsilon_n}(M_{\Delta K})^{\tilde{n}\upsilon_n}_{\tilde{g}\upsilon} \quad (32)$$

the frequency factor for *B* term is

$$B_\theta = (M_{-\Delta K})^{\tilde{n}\upsilon_n}_{\tilde{m}\upsilon_m}(M_{\Delta K})^{\tilde{m}\upsilon_m}_{\tilde{n}\mathrm{v}_\upsilon}\left[\frac{C^R_{K+\Delta K}(J,K)g_n(J+1)}{4(J+1)^2(2J+1)h(\Delta_{mR,K+\Delta K}{}^2+\Gamma_m{}^2)} + \frac{C^Q_{K+\Delta K}(J,K)g_n(J)}{8J^2(J+1)^2h(\Delta_{mQ,K+\Delta K}{}^2+\Gamma_m{}^2)} + \frac{C^P_{K+\Delta K}(J,K)g_n(J-1)}{4J^2(2J-1)(2J+1)h(\Delta_{mP,K+\Delta K}{}^2+\Gamma_m{}^2)}\right] \quad (33)$$

and the frequency factor for *C* term is

$$C_\theta = \upsilon_0 g_n \quad (34)$$

In eqs 24−31, *I* is the intensity of the pumping light with $I = 1/2\epsilon_0 c(E^{(0)})^2$, [38] and all terms of LIOR and LICD are proportional to it, and the signs ± denote the circularity of the pumping optical field.

Equations 24−31 can also be valid for the laser-induced optical rotation and laser-induced circular dichroism of a given rotational level *J* for a linear molecule only if the corresponding factors in the above equations are rewritten as follows:

$$g_m = -\frac{1}{2(2J+1)h}\left[\frac{\Gamma_m}{\Delta_{mR}{}^2+\Gamma_m{}^2} - \frac{\Gamma_m}{\Delta_{iP}{}^2+\Gamma_m{}^2}\right](M_0)^{\tilde{g}\upsilon}_{\tilde{m}\mathrm{v}_m}(M_0)^{\tilde{m}\upsilon_m}_{\tilde{g}\upsilon} \quad (35)$$

$$f_m = -\frac{1}{2(2J+1)h}\left[\frac{\Delta_{mR}}{\Delta_{mR}{}^2+\Gamma_m{}^2} - \frac{\Delta_{mP}}{\Delta_{mP}{}^2+\Gamma_m{}^2}\right](M_0)^{\tilde{g}\upsilon}_{\tilde{m}\upsilon_m}(M_0)^{\tilde{m}\upsilon_m}_{\tilde{g}\upsilon} \quad (36)$$

the frequency factors for LIOR of a linear molecule are

$$A_\phi = -\frac{1}{2(2J+1)h}\left[\frac{v_0{\Delta_{nR}}^2}{[{\Delta_{nR}}^2+{\Gamma_n}^2]^2}-\frac{v_0{\Delta_{nP}}^2}{[{\Delta_{nP}}^2+{\Gamma_n}^2]^2}\right](M_0)^{\tilde{g}v}_{\tilde{n}v_n}(M_0)^{\tilde{n}v_n}_{\tilde{g}v} \tag{37}$$

$$\begin{aligned}B_\phi = {} & (M_0)^{\tilde{g}}_{\tilde{m}v_m}(M_0)^{\tilde{m}v_m}_{\tilde{g}v}(M_0)^{\tilde{n}v_n}_{\tilde{m}v_m}(M_0)^{\tilde{m}v_m}_{\tilde{n}v_n} \\ & \left[\frac{1}{2(2J+1)^2h({\Delta_{mR,K+\Delta K}}^2+{\Gamma_m}^2)}\times\right. \\ & \left(\frac{\Delta_{nR}(J+1)}{{\Delta_{nR}}^2(J+1)+{\Gamma_n}^2}-\frac{\Delta_{nP}(J+1)}{{\Delta_{nP}}^2(J+1)+{\Gamma_n}^2}\right)+ \\ & \frac{1}{2(2J-1)^2h({\Delta_{mP,K+\Delta K}}^2+{\Gamma_m}^2)}\times \\ & \left.\left(\frac{\Delta_{nR}(J-1)}{{\Delta_{nR}}^2(J-1)+{\Gamma_n}^2}-\frac{\Delta_{nP}(J+1)}{{\Delta_{nP}}^2(J+1)+{\Gamma_n}^2}\right)\right]\end{aligned} \tag{38}$$

$$C_\phi = -\frac{1}{2(2J+1)}\left[\frac{v_0\Delta_{nR}}{{\Delta_{nR}}^2+{\Gamma_n}^2}-\frac{v_0\Delta_{nP}}{{\Delta_{nP}}^2+{\Gamma_n}^2}\right](M_0)^{\tilde{g}v}_{\tilde{n}v_n}(\mathrm{M}_0)^{\tilde{n}v_n}_{\tilde{g}v} \tag{39}$$

and the frequency factors for LICD of a linear molecule are

$$A_\theta = -\frac{1}{2(2J+1)h}\left[\frac{v_0\Delta_{nR}\Gamma_n}{[{\Delta_{nR}}^2+{\Gamma_n}^2]^2}-\frac{v_0{\Delta_{nP}}^2\Gamma_n}{[{\Delta_{nP}}^2+{\Gamma_n}^2]^2}\right](M_0)^{\tilde{g}v}_{\tilde{n}v_n}(M_0)^{\tilde{n}v_n}_{\tilde{g}v} \tag{40}$$

$$\begin{aligned}B_\theta = {} & (M_0)^{\tilde{g}v}_{\tilde{m}v_m}(M_0)^{\tilde{m}v_m}_{\tilde{g}v}(M_0)^{\tilde{n}v_n}_{\tilde{m}v_m}(\mathrm{M}_0)^{\tilde{m}v_m}_{\tilde{n}v_n} \\ & \left[\frac{1}{2(2J+1)^2({\Delta_{mR,K+\Delta K}}^2+{\Gamma_m}^2)}\times\right. \\ & \left(\frac{\Gamma_n}{{\Delta_{nR}}^2(J+1)+{\Gamma_n}^2}-\frac{\Gamma_n}{{\Delta_{nP}}^2(J+1)+{\Gamma_n}^2}\right)+ \\ & \frac{1}{2(2J-1)^2({\Delta_{mP,K+\Delta K}}^2+{\Gamma_m}^2)}\times \\ & \left.\left(\frac{\Gamma_n}{{\Delta_{nR}}^2(J-1)+{\Gamma_n}^2}-\frac{\Gamma_n}{{\Delta_{mP}}^2(J+1)+{\Gamma_n}^2}\right)\right]\end{aligned} \tag{41}$$

$$C_\theta = -\frac{1}{2(2J+1)}\left[\frac{v_0\Gamma_n}{{\Delta_{nR}}^2+{\Gamma_n}^2}-\frac{v_0\Gamma_n}{{\Delta_{iP}}^2+{\Gamma_n}^2}\right](M_0)^{\tilde{g}v}_{\tilde{n}v_n}(M_0)^{\tilde{n}v_n}_{\tilde{g}v} \tag{42}$$

Equations 35, 36, 40, and 42 have been obtained when the *A*, *C*, and *D* terms of LICD for a linear molecule are deduced[37] where the vibronic transition moments are not included in the corresponding frequency factors. Also, the formulas and frequency factors of the LIOR and LICD for a linear molecule can apply to an atom if the vibronic transition moments in the frequency factor for a linear molecule are replaced by the electronic transition moments for an atom.

The laser-induced optical activity in eqs 24−31 is in radians, and they can be in another experimental quantity for molar ellipticity[37,43−45] $[\phi_{JK}]$ and $[\theta_{JK}]$; eqs 28−31 can also be expressed in terms of equivalent one ΔA involving absorbance units.[5,37,43]

3. Calculation and Discussion

The MVCD of HCF_3 molecules at 0.5, 1, and 2 cm^{-1} resolution in gas phase have been measured in the experiment of Wang et al. using an infrared vibrational spectrometer in a magnetic field of 8 T.[32d] To know about the magnitude and line shape of the laser-induced optical activity spectra, the resonant circularly polarized pumping optical field is applied to take the place of the magnetic field and to produce the corresponding LIOR and LICD spectra. Note that the IR probing light is circularly polarized for LICD where the differences of absorption for the right and left circularly polarized probing light are detected and is plane-polarized for LIOR where the rotation of the plane of polarization is measured. The parameters of HCF_3 are obtained with the B3LYP/6-311++G** computation,[46] the single LIOR and LICD rotation line for the v_5, *E*-symmetry, CF_3 asymmetric stretching mode[32d] is calculated in section 3.1, and the whole rotational LIOR and LICD spectra for the v_5 mode and the v_1, A_1-symmetry, CH stretching mode[32d] are given in section 3.2.

The experiment is a microwave−IR double resonant consideration where the right circularly polarized pumping microwave optical field with intensity $I = 1$ kW cm^{-2} at the frequency 40.84 GHz is resonant with the rotational transition ($v = 0$, J) → ($v = 0$, J), and the IR probing wave of frequency v_0 with the optical path length $z = 5$ cm scans over the rotational−vibrational absorption transition ($v = 0$, J) → ($v = 1$, J') under the conditions of 298.15 K and 0.3 Torr.[32d] With the B3LYP/6-311++G** computation, the following parameters are obtained. HCF_3 belongs to C_{3v} symmetry, and the ground electronic state is $^1A_1$. The rotational constants are $A = B = 10.21$ GHz and $C = 5.596$ GHz; thus, it is an oblate symmetric top, and the corresponding rotational partition function Z_r is 1.198×10^5 at 298.15 K. The vibration frequencies of the v_5 and v_1 modes are 1125 and 3142 cm^{-1}, respectively. The nonzero permanent dipole moment is 5.920×10^{-30} C m along the molecular *z*-axis. The dipole transition matrix elements of the vibration state are obtained from the derivative of the dipole moment with respect to the Cartesian coordinate.[48] The *x* and *y* transition moments of the v_5 mode from the ground vibrational level to the first excited vibration are both 6.719×10^{-30} C m, and that of the v_1 mode is the *z* transition moment with a value of -2.083×10^{-30} C m. All of the line widths are assumed to be the same magnitude of 0.5 cm^{-1}.[32d] Here, we did not take the influence of line shape of the incident light into account, since the laser line width can be ∼1 MHz.[47]

3.1. Rotationally Resolved LIOR and LICD Line of ($v_5 = 0$, $J = 1$) → ($v_5 = 1$, J'). According to eqs 24−31, the molar elipticities LIOR $[\phi^j_{JK}]$ and LICD $[\theta^j_{JK}]$ ($j = A, B, C, D$; $K = 1$) (Figure 1), $[\phi_{JK}]$ and $[\theta_{JK}]$ ($K = -1, 0, 1$) (Figure 2), and $[\phi_J]$, $[\theta_J]$, and ΔA_J (Figure 3) have been calculated for the rotational−vibrational line ($v_5 = 0$, $J = 1$) → ($v_5 = 1$, J') of HCF_3 molecules and are plotted as a function of the frequency v_0 of the IR probing light. Figures 1−3 show that, in resonant cases, almost all of the LIOR and LICD are of the same order of magnitude for the corresponding terms; the laser-induced optical activity of the *B* term can be as large as that of the *A* and *D* terms with a magnitude of 10 deg cm^2 mol^{-1}, and that of the *C* term is 0.1 deg cm^2 mol^{-1} (see Figure 1); the laser-induced optical activity for the three rotational−vibrational transitions $|v_5 = 0, J = 1, K = -1, 0, 1\rangle \rightarrow |v_5 = 1, J'K'\rangle$ are all on the order of magnitude of 10 deg cm^2 mol^{-1} (see Figure 2), and

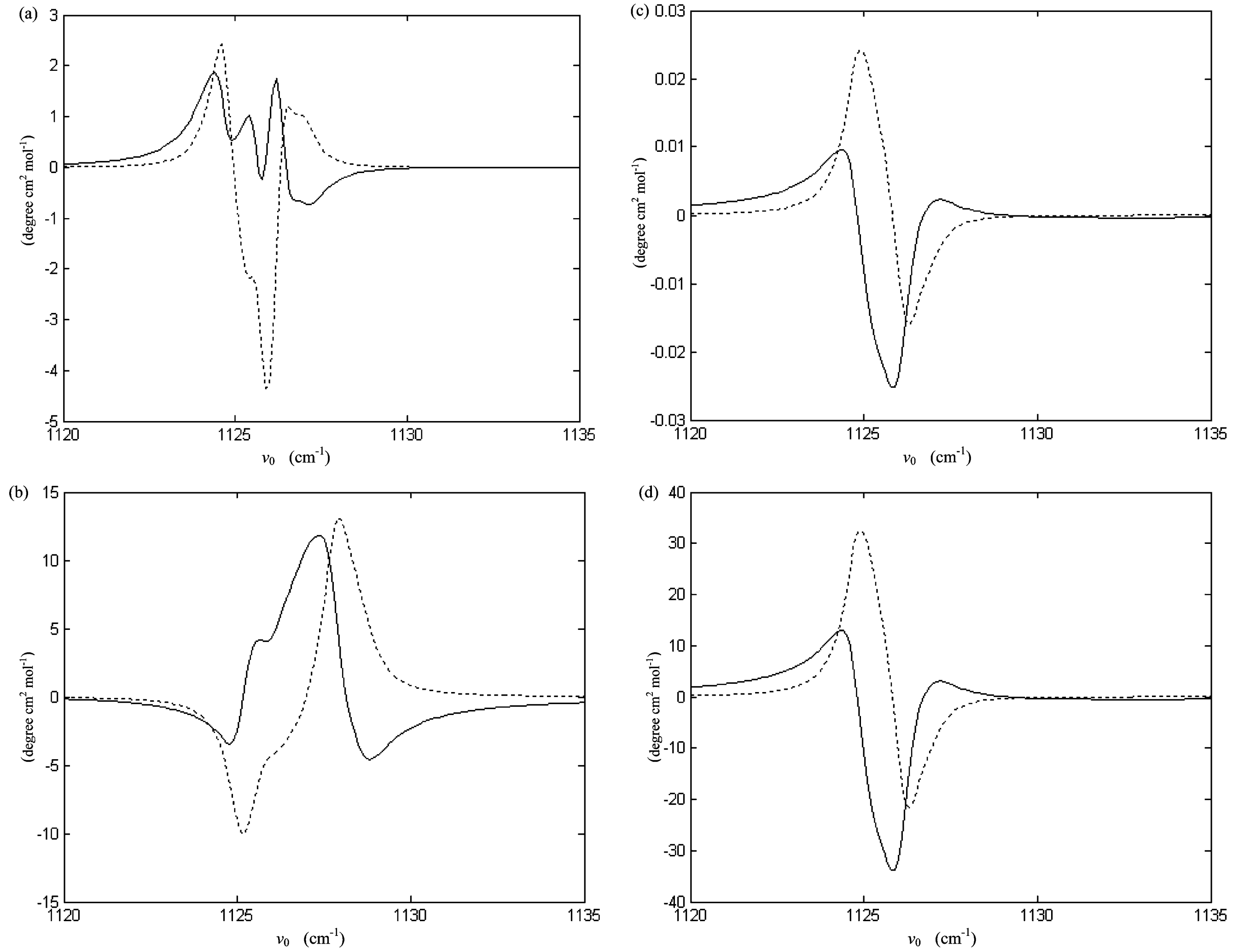

Figure 1. LIOR $[\phi^j_{JK}]$ (solid line) and LICD $[\theta^j_{JK}]$ (dotted line) (j = A, B, C, D) in deg cm^2 mol^{-1} for the rotational−vibrational line ($v_5 = 0$, $J = 1$, $K = 1$) → ($v_5 = 1$, J', K') of HCF$_3$ molecules under the condition of 298.15 K and 0.3 Torr when the probing optical field v_0 sweeps over the vibrational transition ($v_5 = 0$) → ($v_5 = 1$) and the right circularly polarized pumping microwave optical field with intensity $I = 1$ kW cm^{-2} is at the frequency 40.84 GHz resonant with the rotational transition ($v_5 = 0$, $J = 1$) → ($v_5 = 0$, J). (a) $[\phi^A_{JK}]$ and $[\theta^A_{JK}]$ as a function of v_0, (b) $[\phi^B_{JK}]$ and $[\theta^B_{JK}]$ as a function of v_0, (c) $[\phi^C_{JK}]$ and $[\theta^C_{JK}]$ as a function of v_0, (d) $[\phi^D_{JK}]$ and $[\theta^D_{JK}]$ as a function of v_0.

LIOR and LICD for rotational−vibrational transition $|v_5 = 0, J = 1\rangle \rightarrow |v_5 = 1, J'\rangle$ are on the same order of magnitude of 10 deg cm^2 mol^{-1}, and the corresponding absorbance spectra is on the order of magnitude of 10^{-6} (see Figure 3). Out of the absorption region, LIOR and LICD decrease rapidly to zero.

3.2. Rotationally Resolved LIOR and LICD Spectra of ($v_5 = 0$, $J = 1-30$) → ($v_5 = 1$, J') and ($v_1 = 0$, $J = 1-30$) → ($v_1 = 1$, J'). To compare the LICD effect with the rotationally resolved MVCD experiment,[32d] using eqs 24−31, we also calculate the LIOR, LICD, and laser-induced absorbance difference ΔA_J for the rotational−vibrational transitions ($v_5 = 0$, $J = 1-30$) → ($v_5 = 1$, J') and ($v_1 = 0$, $J = 1-30$) → ($v_1 = 1$, J'), which are plotted in Figure 4 and Figure 5, respectively.

Figure 4 shows that the rotationally resolved laser-induced absorbance difference spectra ΔA_J of the v_5 band by the resonant circularly polarized pumping microwave optical field are similar to that of the MVCD spectra, and both of them have a complex band shape (see Figure 3 in ref 32d), and ΔA_J can be 2×10^{-4} when the intensity of the pumping light is 1 kW cm^{-2}. The corresponding MVCD of the v_5 band in the magnetic field of 8 T is 3×10^{-4}.[32d] This indicates that the magnitude of the calculated LICD is comparable with the rotationally resolved MVCD experiment and can be measurable, and so does LIOR, and for the absorbance difference spectra, the pumping light with intensity of 0.1 kW cm^{-2} in LICD is about equivalent to the magnetic field of 1 T in ref 32d.

The v_1 mode of HCF$_3$ has no observable MVCD under their experimental conditions, since the rotational Zeeman g factor of this band is very small ($g \approx 0.03$).[32d] However, Figure 5 shows that for the v_1 band rotationally resolved ΔA_J can be on the order of magnitude of 10^{-4} when the intensity of the pumping light is 1 kW cm^{-2} and can be measurable in comparison with the resolution of the MVCD.[32d] This indicates that the LICD and LIOR for the v_1 mode can be observable and may provide rotational−vibrational information different from the MVCD.

In the above calculations of LIOR and LICD for HCF$_3$ molecules, the intensity of pumping light is 1 kW cm^{-2}, and the corresponding laser-induced shifts by the pumping light are about 20 MHz, which is much smaller than the rotational line width 15 GHz (0.5 cm^{-1}). Thus, it is suitable to apply the perturbation approximation and the rotation-sublevel-unresolved approximation.

Last, it should be noted that, though the expression of the antisymmetric polarizability for a rotational sublevel M of an

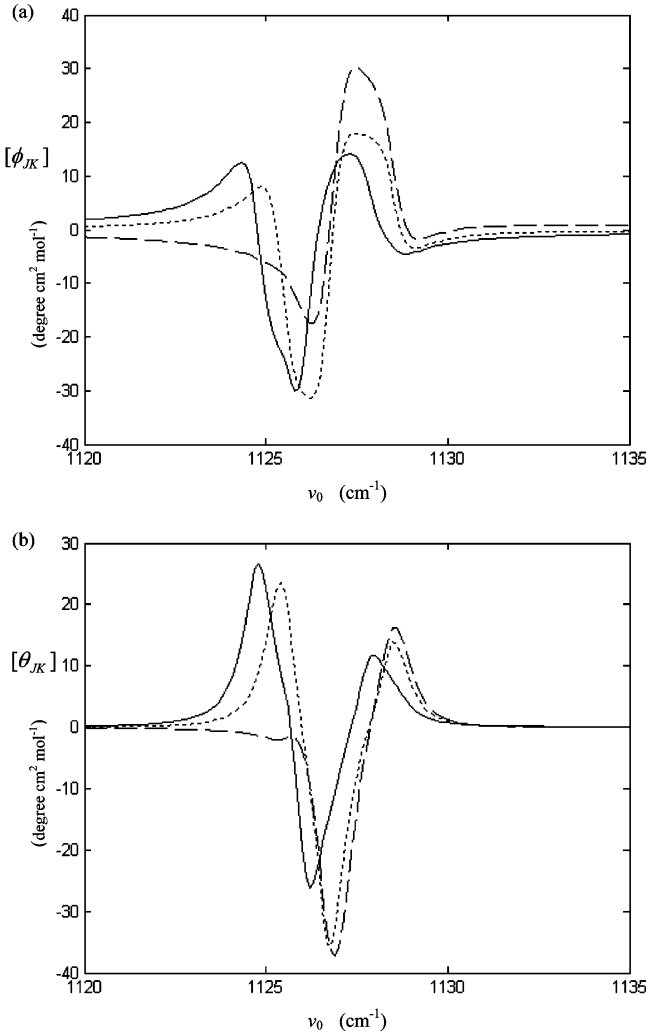

Figure 2. LIOR $[\phi_{JK}]$ and LICD $[\theta_{JK}]$ ($J = 1$, $K = -1$ (dotted line); $K = 0$ (dashed line); and $K = 1$ (solid line)) for the rotational−vibrational line ($\upsilon_5 = 0$, $J = 1$, $K = 0, \pm1$) → ($\upsilon_5 = 1$, J', K') of HCF_3 molecules under the conditions of 298.15 K and 0.3 Torr when the right circularly polarized pumping microwave field with intensity $I = 1$ kW cm^{-2} at the resonant frequency 40.84 GHz. (a) $[\phi_{JK}]$ as a function of υ_0, (b) $[\theta_{JK}]$ as a function of υ_0.

asymmetric top molecule by a resonant circularly polarized optical field is not presented, the rotational antisymmetric polarizability can be nonzero, and the corresponding rotationally resolved LIOR and LICD existent for the wave function of an asymmetric top molecule can be expanded into the complete set of the wave functions of a symmetric top molecule, and a large number of asymmetric top molecules fall under the near-prolate or near-oblate symmetric rotor category, and it is convenient to think in terms of the symmetric rotor limits.[41,49]

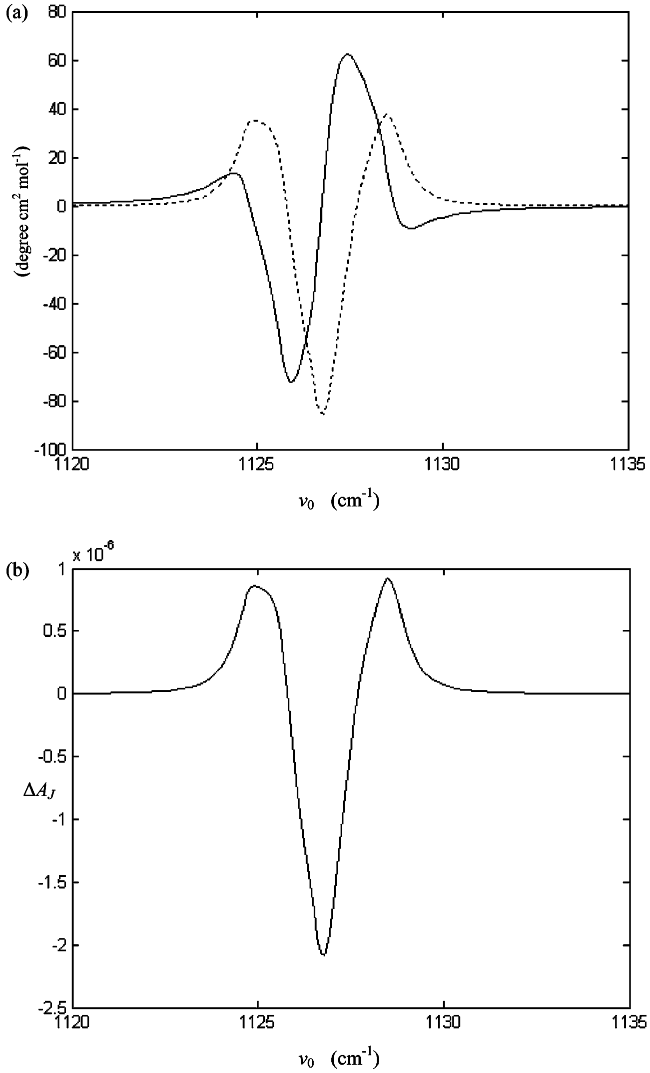

Figure 3. LIOR $[\phi_J]$ and LICD spectra $[\theta_J]$ and ΔA_J ($J = 1$) in 5 cm path length for the rotational−vibrational line ($\upsilon_5 = 0$, $J = 1$) → ($\upsilon_5 = 1$, $J' = J$, $J \pm1$) of HCF_3 molecules under the conditions of 298.15 K and 0.3 Torr when the right circularly polarized pumping microwave field with intensity $I = 1$ kW cm^{-2} at the resonant frequency 40.84 GHz. (a) $[\phi_J]$ (solid line) and $[\theta_J]$ (dotted line) as a function of υ_0, (b) ΔA_J as a function of υ_0.

4. Conclusion

We have discussed the rotationally resolved laser-induced optical activity including the laser-induced optical rotation (LIOR) and laser-induced circular dichroism (LICD) effects of a IR probing light pumped by a collinear intense resonant circularly polarized optical field dependent on the third-order polarizability due to the pure electric dipole interaction for achiral symmetric top molecules in the gas phase. The *B* term of the LIOR and LICD arising from the rotational wave function perturbed by the pumping light is deduced using the semi-classical perturbation theory, and the expressions for the *A*, *C*, and *D* terms, respectively, due to the ac Stark shifts and splittings, the Boltzmann statistical redistribution, and the alteration of occupation probability are obtained on the basis of previous studies.[37] The microwave−IR double resonant spectrum is proposed to detect the LIOR and LICD effects. As an example, the LIOR and LICD for the HCF_3 molecules under the conditions of 298.15 K and 0.3 Torr with 5 cm^{-1} optical length when the IR probing optical sweeps over the rotational−vibrational transition of the υ_5 mode and the right circularly polarized microwave light with intensity of 1 kW cm^{-2} at the frequency 40.84 GHz resonant with the rotational transition ($\upsilon = 0$, J) → ($\upsilon = 0$, J') are calculated using the B3LYP/6-311++G** computation. The results indicate that *B* term can be on the same order of magnitude as the *A* and *D* terms, and the *C* term is 2 orders of magnitude smaller. When comparing the laser-induced absorbance difference ΔA_J with the rotationally resolved MVCD, the LIOR and LICD can be measurable, and the magnitude of LICD with the pumping optical field $I = 0.1$ kW cm^{-2} is equal to that of MVCD with the magnetic field of 1 T. Furthermore, at the same conditions, the calculated results indicate that the observable LIOR and LICD for the υ_1 band

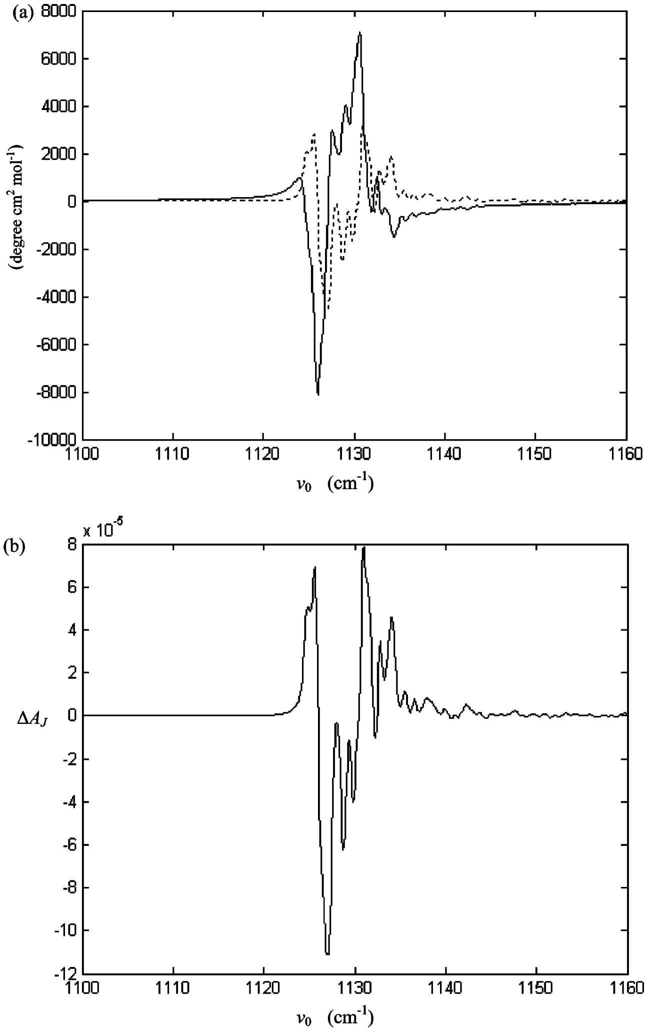

Figure 4. LIOR [ϕ_J] and LICD spectra [θ_J] and ΔA_J ($J = 1-30$) for the rotational−vibrational line ($v_5 = 0$, $J = 1-30$) → ($v_5 = 1$, J') of HCF_3 molecules in 5 cm path length under the conditions of 298.15 K and 0.3 Torr when the right circularly polarized pumping microwave field with intensity $I = 1$ kW cm^{-2} at the resonant frequency 40.84 GHz. (a) [ϕ_J] (solid line) and [θ_J] (dotted line) as a function of v_0, (b) ΔA_J as a function of v_0.

can be obtained though the corresponding MVCD of this band is not detectable. Thus, the LIOR and LICD effect may provide useful new information and form a basis for a different kind of optical activity spectroscopy.

Appendix: Antisymmetric Polarizabilities for the Rotational Sublevel of Symmetric Top Molecules Induced by a Resonant Circularly Polarized Optical Field

With the semiclassical perturbation[1,2] and the angular momentum theory,[42] the nonzero polar vector polarizability $\alpha_{\lambda\mu}$ of the rotational magnetic sublevel $|\tilde{g}v\rangle|JKM\rangle$ induced by a linearly polarized, right circularly polarized, and left circularly polarized optical field at frequency v_0 resonant with the transition between the initial state $|\tilde{g}v\rangle|JKM\rangle$ and the intermediate state $|\tilde{n}v_n\rangle|J'K'M'\rangle$ are $\alpha_{00}(\alpha_0)$, $\alpha_{1-1}(\alpha_+)$, and $\alpha_{1-1}(\alpha_-)$, respectively. All of them can be written into the sum of three terms, α^R ($J' = J + 1$), α^Q ($J' = J$), and α^P ($J' = J - 1$)

$$\alpha_i = \alpha_i^R + \alpha_i^Q + \alpha_i^P \quad i = 0, \pm \tag{A1}$$

The polarizability for the R term induced by a resonant circularly polarized optical field with $\Delta K = 0, \pm 1$ can be expressed in the sum of symmetric and antisymmetric polarizabilities

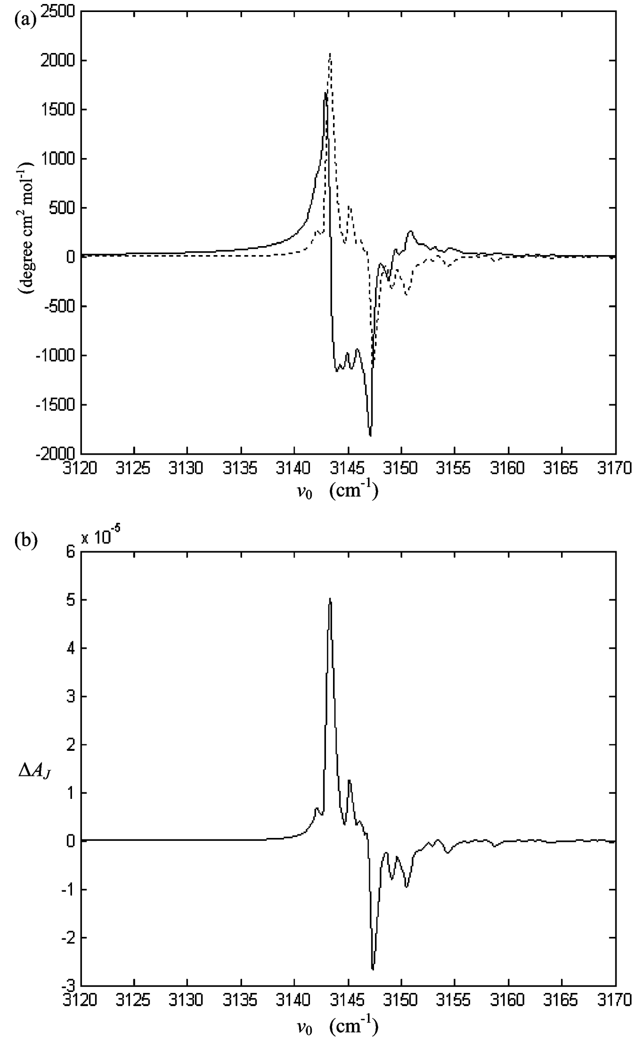

Figure 5. LIOR [ϕ_J] and LICD spectra [θ_J] and ΔA_J ($J = 1-30$) for the rotational−vibrational line ($v_1 = 0$, $J = 1-30$) → ($v_1 = 1$, J') of HCF_3 molecules in 5 cm path length under the conditions of 298.15 K and 0.3 Torr when the right circularly polarized pumping microwave field with intensity $I = 1$ kW cm^{-2} at the resonant frequency 40.84 GHz. (a) [ϕ_J] (solid line) and [θ_J] (dotted line) as a function of v_0, (b) ΔA_J as a function of v_0.

$$\alpha^R_{K+\Delta K,\pm} = \alpha^R_{K+\Delta K,\mathrm{sym}} \mp \alpha^R_{K+\Delta K,\mathrm{ant}} \tag{A2}$$

Here, the symmetric part $\alpha^R_{K+\Delta K,\mathrm{sym}}$ and the antisymmetric part $\alpha^R_{K+\Delta K,\mathrm{ant}}$ are

$$\alpha^R_{K+\Delta K,\mathrm{sym}}(JKM) = C^R_{K+\Delta K}(JK)[(J+1)(J+2) + M^2](f_{R,K+\Delta K} + ig_{R,K+\Delta K}) \tag{A3}$$

$$\alpha^R_{K+\Delta K,\mathrm{ant}}(JKM) = C^R_{K+\Delta K}(JK)[M(2J+3)](f_{R,K+\Delta K} + ig_{R,K+\Delta K}) \tag{A4}$$

where

$$C^R_{K+\Delta K}(JK) = \begin{cases} -2[(J+1)^2 - K^2] & \Delta K = 0 \\ [(J+1)(J+2) \pm K(2J+3) + K^2] & \Delta K = \pm 1 \end{cases}$$

and the frequency factors are

$$f_{R,K+\Delta K} = \frac{\Delta_{R,K+\Delta K}(M_{(-\Delta K)})_{\tilde{n}v_n}^{\tilde{g}v}(M_{\Delta K})_{\tilde{g}v}^{\tilde{n}v_n}}{4(J+1)^2(2J+1)(2J+3)h({\Delta_{R,K+\Delta K}}^2 + {\Gamma_n}^2)}$$

$$g_{R,K+\Delta K} = \frac{\Gamma_n(M_{(-\Delta K)})_{\tilde{n}v_n}^{\tilde{g}v}(M_{\Delta K})_{\tilde{g}v}^{\tilde{n}v_n}}{4(J+1)^2(2J+1)(2J+3)h({\Delta_{R,K+\Delta K}}^2 + {\Gamma_n}^2)}$$

$$\Delta_{R,K+\Delta K} = v_{\tilde{g}v,\tilde{n}v_n} + v_{JK,(J+1)(K+\Delta K)} - v_0 = (v_{\tilde{n}v_n} - v_{\tilde{g}v}) + (v_{(J+1)(K+\Delta K)} - v_{JK}) - v_0$$

Similarly, the symmetric and antisymmetric polarizabilities of the Q and P terms are as follows. The symmetric polarizability $\alpha_{K+\Delta K,\mathrm{sym}}^{Q}$ and the antisymmetric polarizability $\alpha_{K+\Delta K,\mathrm{ant}}^{Q}$ of Q term are

$$\alpha_{K+\Delta K,\mathrm{sym}}^{Q}(JKM) = C_{K+\Delta K}^{Q}(JK)[J(J+1) - M^2](f_{Q,K+\Delta K} + ig_{Q,K+\Delta K}) \quad \text{(A5)}$$

$$\alpha_{K+\Delta K,\mathrm{ant}}^{Q}(JKM) = C_{K+\Delta K}^{Q}(JK)(-M)(f_{Q,K+\Delta K} + ig_{Q,K+\Delta K}) \quad \text{(A6)}$$

where

$$C_{K+\Delta K}^{Q}(JK) = \begin{cases} -2K^2 & \Delta K = 0 \\ J(J+1) \pm K + K^2 & \Delta K = \pm 1 \end{cases}$$

$$f_{Q,K+\Delta K} = \frac{\Delta_{Q,K+\Delta K}(M_{(-\Delta K)})_{\tilde{n}v_n}^{\tilde{g}v}(M_{\Delta K})_{\tilde{g}v}^{\tilde{n}v_n}}{8J^2(J+1)^2h({\Delta_{Q,K+\Delta K}}^2 + \Gamma^2)}$$

$$g_{Q,K+\Delta K} = \frac{\Gamma_n(M_{(-\Delta K)})_{\tilde{n}v_n}^{\tilde{g}v}(\mathrm{M}_{\Delta K})_{\tilde{g}v}^{\tilde{n}v_n}}{8J^2(J+1)^2h({\Delta_{Q,K+\Delta K}}^2 + {\Gamma_n}^2)}$$

$$\Delta_{Q,K+\Delta K} = v_{\tilde{g}v,\tilde{n}v_n} + v_{JK,J(K+\Delta K)} - v_0$$

The symmetric polarizability $\alpha_{K+\Delta K,\mathrm{sym}}^{P}$ and the antisymmetric polarizability $\alpha_{K+\Delta K,\mathrm{ant}}^{P}$ of the P term are

$$\alpha_{K+\Delta K,\mathrm{sym}}^{P}(JKM) = C_{K+\Delta K}^{P}(JK)[J(J-1) + M^2](f_{P,K+\Delta K} + ig_{P,K+\Delta K}) \quad \text{(A7)}$$

$$\alpha_{K+\Delta K,\mathrm{ant}}^{P}(JKM) = C_{K+\Delta K}^{P}(JK)[(-M)(2J-1)](f_{P,K+\Delta K} + ig_{P,K+\Delta K}) \quad \text{(A8)}$$

where

$$C_{K+\Delta K}^{P}(JK) = \begin{cases} -2(J^2 - K^2) & \Delta K = 0 \\ [J(J-1) \pm K(2J-1) + K^2] & \Delta K = \pm 1 \end{cases}$$

$$f_{P,K+\Delta K} = \frac{\Delta_{P,K+\Delta K}(M_{(-\Delta K)})_{\tilde{n}v_n}^{\tilde{g}v}(M_{\Delta K})_{\tilde{g}v}^{\tilde{n}v_n}}{4J^2(2J-1)(2J+1)h({\Delta_{P,K+\Delta K}}^2 + {\Gamma_n}^2)}$$

$$g_{P,K+\Delta K} = \frac{\Gamma_n(M_{(-\Delta K)})_{\tilde{n}v_n}^{\tilde{g}v}(M_{\Delta K})_{\tilde{g}v}^{\tilde{n}v_n}}{4J^2(2J-1)(2J+1)h({\Delta_{P,K+\Delta K}}^2 + {\Gamma_n}^2)}$$

$$\Delta_{P,K+\Delta K} = v_{\tilde{g}v,\tilde{n}v_n} + v_{JK,(J-1)(K+\Delta K)} - v_0$$

In the above equations, $v_{\tilde{g}v,\tilde{n}v_n}$ is the vibronic transition energy, and $v_{JK,J'K'}$ is the rotational transition energy, Γ_n is the dephasing constant for the rotational state of the intermediate state $|\tilde{n}v_n\rangle$, and the vibronic transition moment $(M_{\Delta K})_{\tilde{n}v_n}^{\tilde{g}v} = \langle\tilde{g}v|r_{\Delta K}|\tilde{n}v_n\rangle$. Equations A3−A9 indicate that the polarizability for a rotational sublevel induced by a resonant circularly polarized optical field has not only the symmetric part but also the antisymmetric part, and the antisymmetric polarizability is on the same order of magnitude as the symmetric one.

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