The Quartic Centrifugal Distortion Terms in the Effective Hamiltonian for open-shell complexes

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Abstract

High-resolution spectr oscopy of weakly bound complexes has been widely used to study the nature of intermolecular interactions. Compared with closed-shell complexes, the energy levels and spectra of open-shell complexes are usually more complicated due to the presence of non-zero electron spin and/or electronic orbital angular momentum. A near-rigid rotor model for a nonlinear planar open-shell complex consisting of an open-shell diatomic unit in an electronic state $^{2S+1}\Lambda$ and a closed-shell partner (a rare gas atom or a closed-shell diatomic molecule) has been developed in the literature. Sometimes the quartic centrifugal distortion terms have to be introduced in order to correctly describe experimentally observed energy levels with high J and P quantum numbers. For open-shell complexes with $\Lambda > 0$, those terms of quadratic dependence on J and P were omitted in the expression of the quartic centrifugal distortion terms in the literature, which would lead to contaminated rotational constants A, B, C. Consequently, the molecular geometric structure couldn't be determined reasonably by them.

In this paper, a general expression for the quartic centrifugal distortion terms in the effective Hamiltonian in the Watson S-reduction and Watson A-reduction for open-shell complexes with the open-shell diatomic subunit in an electronic state $^{2S+1}\Lambda$ ($\Lambda > 0$) is derived, taking into account all the operators which give matrix elements of quadratic dependence of L, cubic, and quartic dependence on J and P. Then the non-vanishing matrix elements for the quartic centrifugal distortion terms are derived and listed. Our results are in good agreement with the previous results.

The formula developed in this paper is expected to be useful for analyzing and fitting high-resolution spectra of open-shell complexes in which transitions with high J and P quantum numbers are observed. More physically meaningful rotational constants are expected to be determined along with the quartic centrifugal distortion constants.

Keywords: Open-shell complexes; Quartic centrifugal distortion terms; Effective Hamiltonian; High resolution spectroscopy.

1. Introduction

Recent high-resolution spectroscopic studies on ArNO [2], ArOH [3-8], and NOHF [9] open-shell complexes required the development of theoretical models to interpret the observed spectra and to obtain quantitative or semiquantitative information about inter and intermolecular interactions within this system. Theoretical approaches to these molecular systems began by developing effective Hamiltonians to a near rigid asymmetric rotor taking into account coupling between pure rotational angular momenta due to end over-rotation of the complexes, about its three inertial axes, and unquenched electron-spin and electronic orbital angular momenta of the open-shell diatomic unit. These models neglected effects of free or approximately free internal rotation of diatomic open-shell unit, with the anticipation that bonding between the open-shell group and the closed-shell partner is much more directional than that between two closed-shell partners. Thus, such an approach is expected to give reasonable semiquantitative results when the rotational constant of the diatomic open-shell unit is significantly smaller the barrier height to internal rotation, i.e., when the complex has a well-defined equilibrium geometry.

Nonlinear binary complexes including one open-shell diatomic molecule and one closed-shell partner can be the concept of generically as asymmetric rotors together with unquenched orbital and spin angular momenta and by angular momentum occurring in the internal rotation of the diatomic segment in the complex. The theoretical complications in such systems arise from interactions between the four angular momenta dependence with the electron orbital and spin motions: the overall rotational movement, and the internal rotation motion.

Only the recent two angular momenta happen in rare gas complexes with closed-shell diatomic molecules like Ar-HCl and Ar-HF. However, the critical shaft of theoretical work carried out on Ar-HCl [10-13], for example, clearly describes that the effects of interactions between the overall rotation and the approximately free internal rotation motions are both large and complicated in such systems.

Different theoretical approaches were presented [14-21], on calculations of the rovibronic energy levels and the potential energy surfaces of an open-shell complex including of an open-shell diatomic molecule of $\Lambda \neq 0$, S = 1/2 and a rare gas atom. The theoretical works [15-21], were aimed mainly for analyzing and fitting the observed [6-7], the electronic transition $^2\sum$ - $^2\prod$ of ArOH. Mills et al., [22] published a theoretical work

concerning the microwave transitions of ArNO[2]. Van der Avoird [23] also reported an academic article on the fine structure of O_2 – rare gas Van der Waals complexes. Tennyson and Van der Avoird [24] discussed the impacts of anisotropy on the fine structure of the O_2 – He complex. Beneventi et al. [25], obtained the Ne – O_2 potential energy surface from high-resolution diffraction, scattering, and Zeeman spectrum. Van der Avoird and Brocks [26] reported a theoretical analysis of Van der Waals vibration-rotation– electron spin states of the O_2 – O_2 dimer in its electronic ground state.

Since weakly bonded complexes are often prepared at shallow rotational temperatures (2–4 K), where most of the population is frozen in the rotational states of low J values, the centrifugal distortion terms were ignored entirely in [14, 22]. All the quartic centrifugal distortion terms to a nonlinear open-shell complex in an immoral or a nondegenerate electronic state were introduced in [27, 28]. Analysis of the infrared spectrum of the NOHF complex [9] at a rotational temperature of $2K$ represented that the quartic centrifugal distortion terms D_J and d_1 in Watson's S-reduction[29] are essential for fitting the observed rotational transitions [9]. Fittings of the rotational structure of the detected infrared spectrum of the O_2HF / O_2DF complex [30] and the experimental microwave spectrum of the O_2– SO_2 [31] complex at a rotational temperature of 2κ require the inclusion of all the quartic centrifugal distortion terms in the effective Hamiltonian [28]. The quartic centrifugal distortion terms in Watson's S-reduction [29] were considered [32] in fitting the rotational structure of the observed infrared spectrum of the O_2 – NO_2 complex [33]. These reports [9, 30, 31, 33] demonstrate that the quartic centrifugal distortion terms are necessary for the analysis of the rotational structure of weakly bonded open-shell complexes, even at shallow rotational temperatures.

In the present work, the author suppose theoretical model that take into account centrifugal distortion correction terms in a complex including of a diatomic open-shell unit of $\Lambda = \sum$, $\prod$, Δ , Φ, etc. and S=1/2 (e.g., $X^3 \sum_g^-$ of O_2, $X^3 \sum^-$ and $A^3 \prod_i$ of NH) weakly bonded to a closed-shell partner (e.g., a rare gas atom, HF, CO, etc.). in this model we adopt the rovibronic Hamiltonian of [14] and add to it effective Hamiltonians which take into account the above-mentioned effects. As in [14], we ignore the impact of free internal rotation. The formalism of [14] together with that developed in the present work should be convenient for calculating energy levels, and relative intensities for $^{2S+1}\Lambda$ -$^{2S+1}\Lambda$ and $^{2S+1}\Lambda$ - $^{2S+1}\Lambda$ ($\Lambda \pm 1$) transitions of a planar near rigid rotor including of an open-shell diatomic molecule (in any electronic state $^{2S+1}\Lambda$) weakly bonded to a rare gas atom or closed-shell

diatomic partner. The formalism should also be adequate for semiquantitative calculations if the rotational constant of the open-shell diatomic fragment is small compared to the barrier to internal rotation. If the bending angle is not well defined and the complex has no defined equilibrium geometry, then our approach is inadequate. Under these circumstances: (a) for a triatomic complex formed from an open-shell diatomic molecule in a $\sum$ or a $\prod$ state and a rare gas atom (e.g., NeOH), the convenient model is that of Duberent et al. [34]. (b) In case of a complex containing an open-shell diatomic molecule and a closed-shell diatomic partner, there is no available model to deal with such a system, and ultimately a treatment will be developed for this case. We take into account non-rigidity due to centrifugal forces by adding centrifugal distortion correction terms to the rotational and the electron-spin electron-spin Hamiltonians.

2. Basis Set and Molecular Hamiltonian

We extract the basis set $|v\rangle|L\Lambda\rangle|S, P_s\rangle|P, J, M_J\rangle$ from [14]. Shortly, in this basis set Λ is the projection of the electronic orbital angular momentum along the internuclear axis (z′) of the open-shell diatomic unit. P_S and P is the projections of electron-spin and angular momenta along the axis of least moment of inertia (z). Transmutation among the open-shell diatomic axes x′, y′, z′and the inertial axes x, y, z of the complex, which correspond to the commonly defined A, B, C, inertial axes, respectively, is carried out via the angle θ_1. θ_1 is the angle among the internuclear axis of the diatomic open-shell unit (z′) and the inertial z-axis of the complex. The reason of a diatomic closed-shell partner, an angle θ_2 indicates the angle among the internuclear axis of that closed-shell partner (z″) and the z inertial axis of the complex. The three different axis systems about the angles θ_1 and θ_2 are shown in Figure 1. θ_2 does not affect calculations of rotational energy surfaces, but it does affect comparative intensities of the a, b, and c kind transitions for vibrational transitions focused in the closed-shell diatomic partner.

Hamiltonian in the naught of an external field and omitting nuclear spin has been written as

$$H = H_{rot} + H_{so} + H_q + H_{sr} + H_{ss} + H_{cd} + H_{\lambda d} \qquad (1)$$

H_{rot}, H_{so}, H_q, H_{sr}, H_{ss} and $H_{\lambda d}$ matrix elements are the same as in [14] and they will not be discussed further here, H_{cd} is the quartic centrifugal distortion correction terms in Watson's S-reduction or A-reducton for an asymmetric rotor. We focus our attention on the

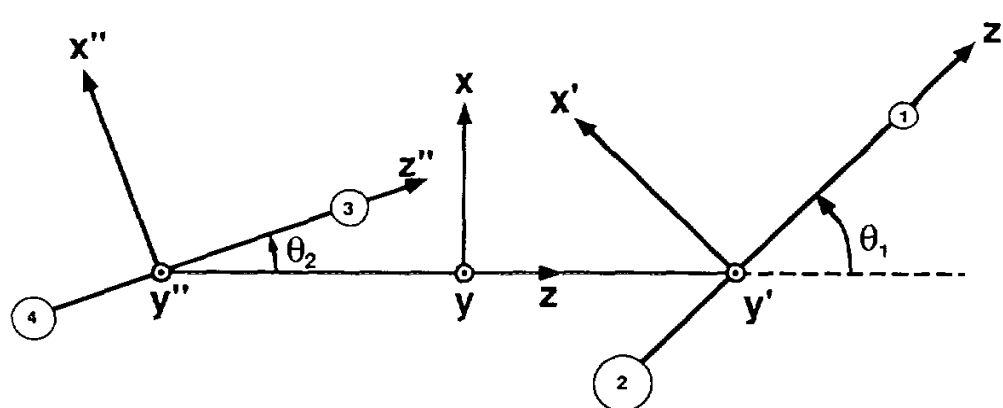operator and matrix elements of the H_{cd} term.

Figure 1: shown a coordinate system for a planar open-shell complex consisting of an open-shell diatomic unit and a closed-shell diatomic partner [27].

The x', y', z' coordinate system is closed to the open-shell diatomic unity wherever the z' axis is along with its atoms marked by 1 and 2. The x'', y'', z'' coordinate system is that of the closed-shell diatomic partner marked by 3 and 4. The x, y, z axes qualify inertial axes of the complex. In this figure, the x, z, x', z', x'' and z'' axes are in the plane of the complex whiles the y, y' and y'' axes are the pointing out the ship. The z - axis is the axis of minimum moment of inertia (A axis) and connects the center of mass of the open-shell unit (1, 2) and the center of mass of the closed-shell partner (3, 4), and the y-axis is the axis of the largest moment of inertia (c-axis). For computing energy levels, expectance quantity of their quantum numbers, and comparative intensities for electronic transitions focused in the open-shell diatomic unit (1, 2), the transformation among the x', y', z' and x, y, z coordinate systems is conveyed through the angle θ_1. For computing comparative intensities of vibrational and rotational transitions focused in the closed-shell partner (3, 4), the transformation between x'', y'', z'' and x, y, z coordinate systems is conveyed through the angle θ_2 the transformation between XYZ and X', Y', Z' coordinates for L_X, $L_{X'}$, L_Z, $L_{Z'}$, S_X, $S_{X'}$, S_Z, $S_{Z'}$ [14, 27]. As shown in Figure 1, the coordinates transformation between L and L' can be related by:

$$L_x = +L_{\acute{x}}cos\theta + L_{\acute{z}}sin\theta$$

$$L_y = L_{\acute{y}}$$

$$L_z = -L_{\acute{x}}sin\theta + L_{\acute{z}}cos\theta \tag{2}$$

Angular momentum components of L and S in either the x, y, z or axis syste x', y', z' m obey the usual angular momentum commutation relation.

3. Quartic Centrifugal Distortion Terms

For a complex of interest, the full treatment of all quadratic, quartic, sextic, and higher order centrifugal distortion terms is quite tedious, even though straightforward. The author only concerned with quartic centrifugal distortion terms which should be adequate for calculating supersonic jet spectra of relatively light triatomic or tetra atomic complexes where rotational levels of J higher than ten are rarely observed, and only the lowest P sublevels are populated. Consequently, we derive the nonvanishing matrix elements of those terms in the $|v\rangle |L\Lambda\rangle |S, P_S\rangle |P, J, M_J\rangle$ basis set for symmetric top "S" reduction and asymmetric top "A" reduction [30].

The quartic centrifugal correction terms hamiltonian In Watson's "S" reduction for an open-shell diatomic molecule van der Waals bonded to a closed partner are given as:

$$H_{cd}^{(s)} = -D_R R^4 - \frac{1}{2} D_{RR_z}(R^2 R_z^2 + R_z^2 R^2) - D_{R_z} R_z^4 + \frac{1}{2} d_1 \left[R^2(R_+^2 + R_-^2) + (R_+^2 + R_-^2)R^2 \right] + d_2(R_+^4 + R_-^4). \quad (3)$$

supposing that $R = J - L - S$, above centrifugal distortion terms are given as

$$H_{cd}^{(s)} = -D_R[(J_x - L_x - S_x)^2 + (J_y - L_y - S_y)^2 + (J_z - L_z - S_z)^2]^2 - \frac{1}{2} D_{RR_z}[(J_x - L_x - S_x)^2 + (J_y - L_y - S_y)^2$$

$$+ (J_z - L_z - S_z)^2](J_z - L_z - S_z)^2 - \frac{1}{2} D_{RR_z}(J_z - L_z - S_z)^2[(J_x - L_x - S_x)^2 + (J_y - L_y - S_y)^2 + (J_z - L_z - S_z)^2]$$

$$- D_{R_z}(J_z - L_z - S_z)^4 + \frac{1}{2} d_1[(J_x - L_x - S_x)^2 + (J_y - L_y - S_y)^2 + (J_z - L_z - S_z)^2][(J_+ - L_+ - S_+)^2 + (J_- - L_- - S_-)^2]$$

$$+ \frac{1}{2} d_1[(J_+ - L_+ - S_+)^2 + (J_- - L_- - S_-)^2][(J_x - L_x - S_x)^2 + (J_y - L_y - S_y)^2 + (J_z - L_z - S_z)^2] + d_2[(J_+ - L_+ - S_+)^4$$

$$+ (J_- - L_- - S_-)^4]. \quad (4)$$

Where J_x, J_y, J_z are componet of the total angular momentum, S_x, S_y, S_z are the component of the electron-spin angular momentum along the principle inertial axes of the complex (x, y, z).

The pure electronic contribution of the centrifugal distortions correction terms is expected to be very small, and the rotation is electronic rotational. Therefore author consider only operators which give matrix elements of quadratic of L, cubic and quartic of J and P. By these reasons L and S are very small, when we do quadratic of S, cubic, quartic and production of these operators they become vanishingly small and almost zero. So neglect the terms that have quadratic of S, cubic, quartic and production of L and S. Thus after expanding and doing some algebic operation in the equation (4), we can obtian the final result as:

$$H_{cd}^{(s)} = -D_R\{(J^2 + L^2)^2 - 2L_{z'}\sin\theta_1(J_+ + J_-)J^2 - 2J^2(J_+S_+ + J_+S_-) - 2L_{z'}\sin\theta_1(J_+ + J_-)L^2 - 2L^2(J_+S_+ + J_+S_-)$$
$$-4J^2(J_zL_{z'}\cos\theta_1 - J_zS_z) - 4L^2(J_zL_{z'}\cos\theta_1 - J_zS_z)\} - D_{RR_z}\{J^2[J_z^2 - 2J_z(L_{z'}\cos\theta_1) - 2J_zS_z] + L^2[J_z^2$$
$$-2J_z(L_{z'}\cos\theta_1) - 2J_zS_z] - \frac{1}{2}(L_{z'}\sin\theta_1)[(J_+ + J_-)J_z^2 + J_z^2(J_+ + J_-)] - \frac{1}{2}[(J_+S_- + J_-S_+)J_z^2 + J_z^2(J_+S_- + J_-S_+)]\}$$
$$-D_{R_z}[J_z^4 - 4J_z^3(L_{z'}\cos\theta_1) - 4J_z^3S_z] - d_1\{3(L_{z'}\sin\theta_1)J^2(J_+ + J_-) + 3J^2(J_+S_+ + J_-S_-) - J^2(J_+^2 + J_-^2)$$
$$-J^2(L_+^2 + L_-^2) - L^2(J_+^2 + J_-^2) - L^2(L_+^2 + L_-^2) + (L_{z'}\sin\theta_1)(J_+^3 + J_-^3) + (J_+^3S_- + J_-^3S_+)\} + d_2[J_+^4 + J_-^4$$
$$-4(L_{z'}\sin\theta_1)(J_+^3 + J_-^3) - 4(J_+^3S_+ + J_-^3S_-) + 6(J_+^2L_-^2 + J_-^2L_+^2)]. \tag{4}$$

The equation (5) is the quartic centrifugal distortion corrections terms equation for Watson's "S" reduction.

In the molecular basis set, matrix elements of the ladder operators satisfy the relations [35, 36].

$$\hat{J}^2 |J, P, M\rangle = \hbar^2 J(J + 1) |J, P, M\rangle \tag{6}$$

$$\hat{J}_Z |J, P, M\rangle = \hbar P |J, P, M\rangle \tag{7}$$

$$\hat{J}_Z\hat{J}_\mp |J, P, M\rangle = \hbar (P \pm 1) |J, P, M\rangle \tag{8}$$

$$\hat{J}_\mp\hat{J}_Z |J, P, M\rangle = \hbar P |J, P, M\rangle \tag{9}$$

$$\langle S, P_s \pm 1 | S_\pm | S, P_S\rangle = [(S \mp P_s)(S \pm P_s + 1)]^{1/2} \tag{10}$$

$$\langle J, P \pm 1 | S_\mp | S, P\rangle = [(J \mp P)(J \pm P + 1)]^{1/2} \tag{11}$$

All the non-vanoshing matrix element of $H_{cd}^{quar\,(S)}$ which are quadratic dependece of **L**, cubic and quartic dependece of **J** and **p** give in the Table 1.

In Watson's "A" reduction, the quartic centrifugal terms can be written as:

$$H_{cd}^{(A)} = -\Delta_R R^4 - \frac{1}{2}\Delta_{RR_z}(R^2R_z^2 + R_z^2R^2) - \Delta_{R_z}R_z^4 - \frac{1}{2}\delta_R\left[R^2(R_+^2 + R_-^2) + (R_+^2 + R_-^2)R^2\right] - \frac{1}{2}\delta_{R_z}[R_z^2(R_+^2 + R_-^2)$$
$$+(R_+^2 + R_-^2)R_z^2]. \tag{11}$$

The quartic centrifugal distortion operators of Δ_R, Δ_{Rz}, Δ_{RRz}, and δ_R, in Eq. (12) are similar to those of D_R, D_{RRz}, D_{Rz}, and d_1, respectively, in the "S" reduction, except that δ_{Rz} and d_2 have opposite signs. However δ_{Rz} and d_2 have different operators. At first, we should derive the quartic centrifugal terms of δ_{R_z}, and subsequently use the value of δ_{Rz} in equation (12), to find the quadratic and quartic centrifugal distortion terms equation for Watson's "A" reduction. For the step by step proof of δ_{Rz}, we consider $R = J - L - S$, and then by expanding the operators, we can write as:

$$-\frac{1}{2}\delta_{R_z}[R_z^2(R_+^2+R_-^2)+(R_+^2+R_-^2)R_z^2]$$

$$=$$

$$-\frac{1}{2}\delta_{R_z}\{[(J_z^2-2(L_{z'}\cos\theta_1)-2J_zS_z)(J_+^2+J_-^2)J_z+(J_+^2+J_-^2)(J_z^2-2(L_{z'}\cos\theta_1)J_z-2J_zS_z)]$$

$$+[(J_z^2-2(L_{z'}\cos\theta_1)-2J_zS_z)(L_+^2+L_-^2)J_z+(L_+^2+L_-^2)(J_z^2-2(L_{z'}\cos\theta_1)J_z-2J_zS_z)]$$

$$-2(L_{z'}\sin\theta_1)[(J_z^2(J_++J_-)+(J_++J_-)J_z^2]-2[J_z^2(J_+S_++J_-S_-)+(J_+S_++J_-S_-)J_z^2]\}. \qquad (12)$$

Now we substitute the value of δ_{Rz} which is equation (13) in equation (12) and find quartic centrifugal distortion terms for Watson's "A" reduction. Therefore we can write the final result of quartic centrifugal distortion terms for Watson's "A" reduction as in (14).

$$H_{cd}^{(A)}=-\Delta_R\{(J^2+L^2)^2-2L_{z'}\sin\theta_1(J_++J_-)J^2-2J^2(J_+S_++J_+S_-)-2L_{z'}\sin\theta_1(J_++J_-)L^2-2L^2(J_+S_++J_+S_-)$$

$$-4J^2(J_zL_{z'}\cos\theta_1-J_zS_z)-4L^2(J_zL_{z'}\cos\theta_1-J_zS_z)\}-\Delta_{RR_z}\{J^2[J_z^2-2J_z(L_{z'}\cos\theta_1)-2J_zS_z]+L^2[J_z^2$$

$$-2J_z(L_{z'}\cos\theta_1)-2J_zS_z]-\frac{1}{2}(L_{z'}\sin\theta_1)[(J_++J_-)J_z^2+J_z^2(J_++J_-)]-\frac{1}{2}[(J_+S_-+J_-S_+)J_z^2+J_z^2(J_+S_-+J_-S_+)]\}$$

$$-\Delta_{R_z}[J_z^4-4J_z^3(L_{z'}\cos\theta_1)-4J_z^3S_z]-\delta_R\{3(L_{z'}\sin\theta_1)J^2(J_++J_-)+3J^2(J_+S_++J_-S_-)-J^2(J_+^2+J_-^2)$$

$$-J^2(L_+^2+L_-^2)-L^2(J_+^2+J_-^2)-L^2(L_+^2+L_-^2)+(L_{z'}\sin\theta_1)(J_+^3+J_-^3)+(J_+^3S_-+J_-^3S_+)\}-\frac{1}{2}\delta_{R_z}\{[(J_z^2$$

$$-2(L_{z'}\cos\theta_1)-2J_zS_z)(J_+^2+J_-^2)J_z+(J_+^2+J_-^2)(J_z^2-2(L_{z'}\cos\theta_1)J_z-2J_zS_z)]+[(J_z^2-2(L_{z'}\cos\theta_1)$$

$$-2J_zS_z)(L_+^2+L_-^2)J_z+(L_+^2+L_-^2)(J_z^2-2(L_{z'}\cos\theta_1)J_z-2J_zS_z)]-2(L_{z'}\sin\theta_1)[(J_z^2(J_++J_-)+(J_++J_-)J_z^2]$$

$$-2[J_z^2(J_+S_++J_-S_-)+(J_+S_++J_-S_-)J_z^2]\}. \qquad (13)$$

All the non-vanoshing matrix element of $H_{cd}^{quar\,(A)}$ which are quadratic dependece of **L**, cubic and quartic dependece of **J** and **P** give in the Table 2.

table 1 is the quartic and quaratic centrifugal distortion terms non-vanishing matirix elements for $H_{cd}^{quar(S)}$.

1. $\langle \eta, L, \Lambda, S, P_s, J, P, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = - D_R \{ [(J(J+1)^2 + L(L+1)^2] - 4PP_s[J(J+1) + L(L+1)] + 4P(\Lambda \cos\theta_1)$
$[J(J+1) + L(L+1)] - D_{RR_z}\{[J(J+1) + L(L+1)]P^2 - 2(\Lambda \cos\theta_1)P$
$[J(J+1) + L(L+1)] - 2PP_s[J(J+1) + L(L+1)] - D_{R_z}[P^4 - 4P^3(\Lambda \cos\theta_1) - 4P^3 P_s]$

2. $\langle \eta, L, \Lambda, S, P_s, J, P \pm 1, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = (\Lambda \sin\theta_1)\{2D_R[J(J+1) + L(L+1)] + \frac{1}{2}D_{RR_z}[P^2 + (P \pm 1)^2] - 3d_1[J(J+1)]\}$
$[(J \mp P)(J \pm P + 1)]^{1/2}$

3. $\langle \eta, L, \Lambda, S, P_s, J, P \pm 2, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = d_1\{[J(J+1) + L(L+1)][(J \mp P)(J \pm P + 1)(J \mp P - 1)(J \pm P + 2)]^{1/2}\}$

4. $\langle \eta, L, \Lambda \pm 2, S, P_s, J, P, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = d_1[J(J+1) + L(L+1)][(L \mp \Lambda)(L \pm \Lambda + 1)(L \mp \Lambda - 1)(L \pm \Lambda + 2)]^{1/2}$

5. $\langle \eta, L, \Lambda, S, P_s \pm 1, J, P \pm 1, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = \{2D_R[J(J+1) + L(L+1)] + \frac{1}{2}D_{RR_z}[P^2 + (P+1)^2]\}\{[(S \mp P_S)(S \pm P_S + 1)]^{1/2}$
$[(J \mp P)(J \pm P + 1)]^{1/2}\}$

6. $\langle \eta, L, \Lambda, S, P_s \pm 1, J, P \mp 1, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = -3d_1[J(J+1)][(J \pm P)(J \mp P + 1)]^{1/2}[(S \mp P_s)(S \pm P_s + 1)]^{1/2}$

7. $\langle \eta, L, \Lambda \pm 2, S, P_s, J, P \mp 2, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = 6d_2[(L \mp \Lambda)(L \pm \Lambda + 1)(L \mp \Lambda - 1)(L \pm \Lambda + 2)]^{1/2}[(J \pm P)(J \mp P + 1)$
$(J \pm P - 1)(J \mp P + 2)]^{1/2}$

8. $\langle \eta, L, \Lambda, S, P_s, J, P \pm 3, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = -(\Lambda \sin\theta_1)[d_1 + 4d_2][(J \mp P)(J \pm P + 1)(J \mp P - 1)(J \pm P + 2)$
$(J \mp P - 2)(J \pm P + 3)]^{1/2}$

9. $\langle \eta, L, \Lambda, S, P_s \pm 1, J, P \pm 3, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = -d_1[(S \mp P_S)(S \pm P_S + 1)]^{1/2}[(J \mp P)(J \pm P + 1)(J \mp P - 1)$
$(J \pm P + 2)(J \mp P - 2)(J \pm P + 3)]^{1/2}$

10. $\langle \eta, L, \Lambda, S, P_s \pm 1, J, P \mp 3, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = -4d_2[(S \mp P_S)(S \pm P_s + 1)]^{1/2}[(J \pm P)(J \mp P + 1)(J \pm P - 1)$
$(J \mp P + 2)(J \pm P - 2)(J \mp P + 3)]^{1/2}$

11. $\langle \eta, L, \Lambda, S, P_s, J, P \pm 4, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = d_2[(J \mp P)(J \pm P + 1)(J \mp P - 1)(J \pm P + 2)(J \mp P - 2)$
$(J \pm P + 3)(J \mp P - 3)(J \pm P + 4)]^{1/2}$

The above matrix elements are those of the centrifugal distortion Hamiltonian $H_{cd}^{quar\,(S)}$ for the "S" reduction given in equation (5). The angle θ_1 the same as defined in figure 1. The above matrix elements are only those of D_R wich have quadratic depends of L, cubic and quartic depends of J, D_{RR_Z} which have quaratic depends of L, cubic and quartic of depends of JP; D_{R_Z} which have cubic and quartic depends of P, d_1 which are cubic on P, d_2 which are quadratic on L, cubic and quartic on J.

table 2 is the quartic and quaratic centrifugal distortion terms non-vanishing matirix elements for $H_{cd}^{quar(A)}$.

1. $\langle \eta, L, \Lambda, S, P_s, J, P, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = -\Delta_R\{[(J(J+1)^2 + L(L+1)^2] - 4PP_s[J(J+1) + L(L+1)]$
$+ 4P(\Lambda\cos\theta_1)[J(J+1) + L(L+1)] - \Delta_{RR_z}\{[J(J+1)$
$+ L(L+1)]P^2 - 2(\Lambda\cos\theta_1)P[J(J+1) + L(L+1)] - 2PP_s$
$[J(J+1) + L(L+1)] - \Delta_{R_z}[P^4 - 4P^3(\Lambda\cos\theta_1) - 4P^3P_s]$

2. $\langle \eta, L, \Lambda, S, P_s, J, P\pm1, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = (\Lambda\sin\theta_1)\{2\Delta_R[J(J+1) + L(L+1)] + \frac{1}{2}\Delta_{RR_z}[P^2 + (P\pm1)^2]$
$+ 3\delta_R[J(J+1)] - \delta_{R_z}[P^2 + (P\pm1)^2]\}[(J\mp P)(J\pm P+1)]^{1/2}$

3. $\langle \eta, L, \Lambda, S, P_s, J, P\pm2, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = -\delta_R\{[J(J+1) + L(L+1)] - \frac{1}{2}\delta_{R_z}\{P^2 + (P\pm2)^2$
$+ 2(\Lambda\sin\theta_1)[P + (P\pm2)] + 2[PP_s + (P\pm2)(P_s\pm2)]\}$
$[(J\mp P)(J\pm P+1)(J\mp P-1)(J\pm P+2)]^{1/2}\}$

4. $\langle \eta, L, \Lambda\pm2, S, P_s, J, P, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = \delta_R[J(J+1) + L(L+1)] - \frac{1}{2}\delta_{R_z}\{P^2 + (P\pm2)^2 + 2(\Lambda\sin\theta_1)$
$[P + (P\pm2)] + 2[PP_s + (P\pm2)(P_s\pm2)]\}$
$[(L\mp\Lambda)(L\pm\Lambda+1)(L\mp\Lambda-1)(L\pm\Lambda+2)]^{1/2}$

5. $\langle \eta, L, \Lambda, S, P_s\pm1, J, P\pm1, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = \{2\Delta_R[J(J+1) + L(L+1)] + \frac{1}{2}\Delta_{RR_z}[P^2 + (P+1)^2]\}$
$\{[(S\mp P_s)(S\pm P_s+1)]^{1/2}[(J\mp P)(J\pm P+1)]^{1/2}\}$

6. $\langle \eta, L, \Lambda, S, P_s\pm1, J, P\mp1, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = \{3\delta_R[J(J+1)] + \delta_{R_z}[P^2 + (P\mp1)^2][(J\pm P)(J\mp P+1)]^{1/2}$
$[(S\mp P_s)(S\pm P_s+1)]^{1/2}$

8. $\langle \eta, L, \Lambda, S, P_s, J, P\pm3, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = \delta_R(\Lambda\sin\theta_1)[(J\mp P)(J\pm P+1)(J\mp P-1)(J\pm P+2)$
$(J\mp P-2)(J\pm P+3)]^{1/2}$

9. $\langle \eta, L, \Lambda, S, P_s\pm1, J, P\pm3, M_J | H_{cd} | \eta, L, \Lambda, S, P_s, J, P, M_J \rangle = \delta_R[(S\mp P_s)(S\pm P_s+1)]^{1/2}[(J\mp P)(J\pm P+1)(J\mp P-1)$
$(J\pm P+2)(J\mp P-2)(J\pm P+3)]^{1/2}$

All the matrix elements of $H_{cd}^{quar\,(A)}$ for the "A" reduction given in equation (14). The differences between these non-vanishing matrix elements and those of for the "S" reduction given in table 1 are that d_1 of table 1 is substituted here by δ_R, d_2 and matrix elements assiciated with it are omitted in this table and matrix elements of operators of δ_{R_z} given in equation (13) are included in this table.

5. Conclusion

In this paper, I have derived the correction terms for the effective Hamiltonians (H_{cd}) in nearly complete formulas quadratic and quartic centrifugal distortion terms in the effective Hamiltonian for an open-shell diatomic molecule weakly bonded to closed-shell partner. The matrix elements of these Hamiltonians are valid for a near rigid planar open-shell complex consisting of a diatomic open-shell unit described by $^{2S+1}\Lambda$ and a closed-shell partner. The complex was assumed to have a well-defined equilibrium geometry, so I can safely ignore the effects of large amplitude motion.

I also derive the non-vanishing matrix elements of quadratic and quartic centrifugal distortion correction terms for an open-shell diatomic molecule van der Waals bonded to a close partner for Watson's "S" and Watson's "A" reduction. The model presented here is quite promising in understanding infrared transitions observed in some complexes like O_2-HF and in analyzing and fitting high-resolution electronic,

vibrational, and microwave spectra of a weakly bonded complex that consists of open-shell diatomic molecule in a $^{2S+1}\sum$ electronic state, with $S \geq 1/2$, and a closed-shell partner; a rare gas atom or a diatomic molecule or a planar polyatomic molecule.

For future studies, the non-vanishing matrix elements presented in Tables 1 and 2 could be implemented in computer code to calculate the rotational energy levels or a vibrational transition that is either localized in the open-shell diatomic molecule or the closed-shell partner. Such a system can be used as a testing ground for the analytical calculations against the observed IR spectrum and observed microwave spectrum of some complexes.

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