Studies on the electric dipole moment function and line parameters for high overtone bands of NO

Huajun Chen [a], Xin Lu Cheng [a,*], Hao Liu [b], Jie Wu [b]

[a] Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, People's Republic of China
[b] Science and Technology on Optical Radiation Laboratory, Beijing 100854, People's Republic of China

ARTICLE INFO

ABSTRACT

An accurate electric dipole moment function (EDMF) has been obtained by fitting the best available data including the pure rotational band 0–0 for individual ro-vibrational transitions for nitric oxide. Line intensities calculated using the fitted EDMF agree better with the measurements than the current HITRAN database. Moreover, the accurate ab initio potential energy curve (PEC) and EDMF were found using the multi-reference averaged quadratic coupled-cluster (AQCC) approach with the basis set aug-cc-pV6Z (aV6Z). The good agreement of the vibrational transition moments, computed using the Rydberg–Klein–Rees (RKR) potential and the fitted EDMFs, with experiments shows the present fitted EDMF could be more accurate than other fitted ones at the valid range. Our ab initio vibrational transition moments agree better with experimental data than the ones calculated using the previous theoretical PEC and EDMF, especially at the high overtones. We expect that the present study will be helpful for the transitions including high υ and high overtone bands of NO.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Nitric oxide $^{14}N^{16}O$ (hereafter NO) plays an important role in astrophysics, physical chemistry, and environmental science. NO nightglow has been observed in three planets: Earth [1,2], Mars [3,4], and Venus [5,6]. NO gas is poisonous and can cause severe environmental pollution, including water, soil and air pollution. Because of their importance, spectral parameters of NO have been included in the HITRAN spectroscopic database [7] from the early edition [8]. In the most recent HITRAN compilation, the intensities were based on a combination of the experimental and theoretical electric dipole moment function (EDMF); the details of data in HITRAN can be found in Goldman et al. [9]. Recently, we found that some high

overtone band intensities of the HITRAN database disagree with the recent experimental results. It indicates that the EDMF might not be accurate enough and not be fit to evaluate the line intensities for high overtone bands.

Some experimental and semi-empirical EDMFs of the molecule NO obtained by deducing various experimental data with different methods were conducted in the papers [10–18]. Comprehensive ab initio theoretical calculations of EDMFs for NO ($X^2\Pi$) were also performed by Billingsley et al. [19,20], Langhoff et al. [21,22], and de Vivie and Peyerimhoff [23]. A combination of experimental EDMF by Spencer et al. [15] and theoretical EDMF by Langhoff et al. [22] and Holtzclaw et al. [24] was used in HITEMP 2010 [25]. The vibrational transition moments (or rotationless dipole moments) calculated using these EDMFs always disagree with the experimental results of the high overtone bands. Recently based on the experimental measurements of line intensities from the first to the fifth overtone using Fourier transform spectroscopy, Lee et al. [26]

derived an EDMF valid from $1.0 \leq r \leq 1.38$ Å. Bood et al. [27] used their value of the vibrational transition moment for the sixth overtone, together with recent experimental determinations from the literature of lower overtone intensities over a wide range of vibrational levels, to determine an EDMF valid for $0.91 \leq r \leq 1.74$ Å. Although the vibrational transition moment calculated using these EDMFs from Lee et al. and Bood et al. can agree well with the experiments, there still exist shortcomings of accuracy. More research is needed for the EDMF of NO ($X^2\Pi$).

On the one hand, there exists a standard method of determining the vibrational transition moment for the ro-vibrational bands by fitting the existing experimental data. Then these vibrational transition moments are employed in a second step to determine the polynomial coefficients of EDMF [13–15]. In order to utilize the individual high-quality measurements for line intensities, we adopted a direct fit approach to determine the EDMF for NO in this work. The ro-vibrational line intensities derived from the present fitted EDMF were compared to experimental data and HITRAN. On the other hand, as the techniques of a curve fit are always tied to experimental data, which are only part and incomplete, ab initio quantum chemical techniques are also particularly useful to calculate reliable EDMF. In this work, we performed a series of theoretical calculations to determine the EDMF of NO ($X^2\Pi$). Ultimately, the vibrational transition moments obtained using the present fitted EDMF and the theoretically calculated EDMFs were compared with previous experimental data.

2. Theoretical basis

2.1. Fitted method of the electric dipole moment function

The EDMF of a diatomic molecule can be written as a Taylor expansion as follows:

$$M(r) = M_0 + M_1 x + M_2 x^2 + \cdots + M_i x^i + \cdots \tag{1}$$

where $x = (r - r_e)/r_e$, r_e is the equilibrium separation, M_0 represents the permanent dipole moment at the minimum of the potential, where $r = r_e$. In a harmonic potential, the linear moment $M_1 x$ results in $\Delta v = 1$ transitions, while the quadratic moment $M_1 x^2$ results in $\Delta v = 2$ transitions, etc. Therefore, experimental data of the higher overtone intensities can provide the information on the higher moments of $M(r)$. In an anharmonic oscillator system, the intensity of a certain overtone is actually determined by both the shapes of EDMF and the mechanical anharmonicity potential [27].

Tipping and Herman [28] developed an approach to determine the EDMF using only the pure vibrational transition moments. In order to obtain the vibrational transition moment, one can make use of the available line intensities and fit them separately for every band to the Herman–Wallis expression as follows [29]:

$$|\langle v', J'|M(r)|v'', J''\rangle|^2 = |\langle v', 0|M(r)|v'', 0\rangle|^2 (1 + Cm + Dm^2 + \cdots) \tag{2}$$

where $\langle v', 0|M(r)|v'', 0\rangle$ was used as the vibrational transition moment $\mu_{v',v''}$, C and D are the Herman–Wallis coefficients,

with $m = -J$ for the P-branch and $J+1$ for the R-branch. In order to derive the M_i coefficients from Eq. (1), these obtained vibrational transition moments are then fit to

$$\langle v', 0|M(r)|v'', 0\rangle = \sum_i M_i \langle v', 0|x^i|v'', 0\rangle \tag{3}$$

where the expectation values $\langle v', 0|x^i|v'', 0\rangle$ can be determined from the potential energy function. The single and double primes correspond to upper and lower state, respectively. Both Lee et al. [26] and Bood et al. [27] adopted this approach to derive the EDMF.

In 2001, Kiriyama et al. [30] suggested that the inclusion of rotational components into the fit can allow for a better determination of the M_i coefficients by fitting to a larger number of points

$$\langle v', J'|M(r)|v'', J''\rangle = \sum_{i=1}^{n} M_i \langle v', J'|x^i|v'', J''\rangle \tag{4}$$

where $\langle v', J'|M(r)|v'' J''\rangle$ was not the directly calculated value of the individual line intensity, but was the fitted value obtained from a polynomial fit of experimental values. In their work, the measured bands of HCl had $v'' = 0$ as a lower state. Li et al. [31] developed this direct fit approach by using the direct ro-vibrational transitional moments computed using experimental line intensities and asserted their superiority.

2.2. Theoretical computational details

NO is an open-shell molecule and the electric config-uration of NO ($X^2\Pi$) is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi_x^2 1\pi_y^2 2\pi_x^1/2\pi_y^1$, which has b_1 or b_2 symmetry. The PECs and EDMFs were computed using highly correlated ab initio methods, namely, the complete active space self-consistent field (CASSCF) [32] approach followed by the highly accurate AQCC method [33,34]. To investigate the effect of basis sets on the potential curves and dipole moments, we employed separately the augmented triple-zeta (aug-cc-pVTZ), quadruple-zeta (aug-cc-pVQZ), quintuple-zeta (aug-cc-pV5Z), and sextuple-zeta (aug-cc-pV6Z) basis sets (denoted by aVTZ, aVQZ, aV5Z and aV6Z, respectively, discussed later in this paper) of Dunning and colleagues [35–37] for both N and O atoms. Throughout the present work, we only considered the electronic correlation energy of valence electrons and only chose an active space: the full valence active spaces consist of eight valence orbitals $3\sigma 4\sigma 5\sigma 1\pi_x 1\pi_y 2\pi_x 2\pi_y 6\sigma$, denoted by (4220) in C_{2v} point-group symmetry. The calculations are performed using the MOLPRO 2009.1 program package [38].

Using Le Roy's LEVEL 8.0 program [39], the transition moments were calculated by combining the fitted EDMFs and a RKR potential energy function, or by combining the ab initio PEC and EMDF obtained by the same method and basis set level. In all our work, the RKR potential curves for NO were constructed using the pure numerical RKR method [40] with the Dunham coefficients from Amiot [41], which provided accurate molecular parameters for higher-lying vibrational levels (up to $v = 22$).