Journal of Molecular Structure 993 (2011) 431–434

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

A theoretical study of the vibrational spectrum of maleimide

Eduardo C. Aguiar [*], João Bosco P. da Silva, Mozart N. Ramos

Departamento de Química Fundamental, Universidade Federal de Pernambuco (UFPE), 50670-901 Recife (PE), Brazil

ARTICLE INFO

Article history:
Available online 3 November 2010

Keywords:
Maleimide
Vibrational spectrum
Theoretical calculations
Infrared spectrum
Anharmonicity

ABSTRACT

B3LYP and MP2 theoretical calculations with 6-31++G(d,p) basis set have been performed to interpret the infrared spectrum of maleimide. The anharmonicity effect has been included to correct the calculated harmonic frequency values. As expected, this has allowed a better agreement with the experimental ones, especially B3LYP values. The more pronounced changes have been verified to the X—H (X = C or N) stretching modes.

The calculated IR intensities compare favorably well with their corresponding relative experimental values in vapor phase. The large discrepancy is found to the symmetric C—C stretching mode of the heterocyclic ring. It appears to be a strong band at 897 cm^{-1}, in contrast to B3LYP and MP2 calculated values. The calculated intensities due to the out-of-plane and in-plane bending and stretching modes for the X—H oscillators (X = C or N) have been adequately interpreted in terms of hydrogen atomic charges and X—H charge-fluxes extracted from the modified charge–charge flux-overlap model (CCFOM) for infrared intensities.

1. Introduction

Maleimide (Fig. 1) and its *N*-derivatives have been employed in a variety of photochemical applications, which are based on their electron accepting properties [1]. Indeed, this represents the basis for modulating the fluorescence of compounds in which maleimide is incorporated. As a consequence, this modulation can be used to probe polymerization dynamics [2] or as a molecular sensor [3].

Nowadays, it is already well established that maleimide possesses a planar structure with C_{2v} symmetry [4]. It is interesting to point out that this planarity can be important to a possible biological activity of maleimide, once it has a molecular and electronic structure very similar to phthalimide. This latter is known to be a potent hypolipidemic agent. The lost of this planarity of the five-membered ring reduces, enormously, the hypolipidemic action in phthalimide [5].

In the last years, the chemistry of maleimide has been largely studied through combined studies involving vibrational spectroscopy and theoretical calculations [6–10]. In particular, Parker and collaborators [7] have combined infrared, Fourier Transform-Raman (FT-Raman), Inelastic Neutron Scattering (INS) spectroscopies and DFT calculations to provide the vibrational assignments of the spectra of maleimide and its *N*-derivatives. Barnes and collaborators [11] have also reported the infrared and Raman spectra for maleimide, *N*-deuterated maleimide and maleic anhydride in argon and nitrogen matrices and in the solid phase at 20 K. Furthermore, they have investigated the interaction of maleimide with nitrogen, water and hydrogen chloride. This analysis has shown that water and hydrogen chloride form hydrogen-bonded complexes with a carbonyl group of the maleimide, whereas nitrogen interacts with the NH group. As a result, it is now well established that maleimide is expected to be monomeric only in the vapor phase and in dilute solutions [10], in contrast to what is found in maleic anhydride [12], which must be monomeric in all aggregation states. On the other hand, maleimide is expected to form dimer in concentrated solutions, melting and crystals [10], similarly to what happens with succinimide [13]. Recently, we have studied the effect of the H-bond formation in the molecular properties of maleimide in order to estimate the H-bond strength, frequency shifts and intensity enhancements after complexation [14].

This work aims to interpret the vibrational spectrum of maleimide using MP2 [15] and B3LYP [16] calculations with 6-31++G(d,p) basis set [17] through the Gaussian 03 program [18]. Here we have also analyzed the anharmonicity effect [19] on the molecular geometry and vibrational frequencies of maleimide, whereas its infrared intensities have been interpreted using the modified charge–charge flux-overlap model (CCFOM) [20,21].

2. Results and discussion

In Table 1 we give the optimized geometries with and without anharmonicity correction for maleimide using the MP2 and B3LYP levels of calculation with a 6-31++G(d,p) basis set. There we also include its available experimental values obtained from the

---

[*] Corresponding author. Tel.: +55 81 21265007.
E-mail address: castro.eduardo@gmail.com (E.C. Aguiar).

0022-2860/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2010.10.042

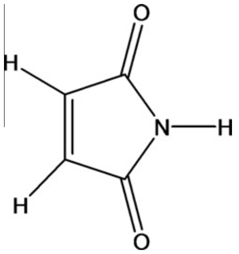

Fig. 1. Maleimide structure.

electron diffraction study in the gas phase [4]. In general, there is a good agreement between theoretical and experimental values. Except to N—H bond, the anharmonicity correction increases the chemical bond length for both the MP2 and B3LYP levels of calculation. This provokes a better agreement with the corresponding experimental values. The bond angles, in turn, practically are not affected by this correction.

2.1. Vibrational analysis

In Table 2 we show the vibrational assignments and frequencies, as well as infrared intensities of maleimide obtained from B3LYP and MP2 calculations using a 6-31++G(d,p) basis set. The anharmonicity effect on the vibrational frequencies is also shown in this Table, whereas experimental values in gas phase [10] and in argon matrix at 20 K [11] are also given for comparison. The 21 active IR fundamentals can be divided into $9a_1 + 4b_1 + 8b_2$. Initially, we can observe, from Table 2, that there is a good agreement between experimental and calculated spectra of maleimide, especially when the anharmonicity correction is introduced on the calculated values.

In order to better analyze these active IR modes of maleimide, we will divide its IR spectrum into three parts: (a) the region of the X—H stretching modes with X = C and N, (b) the region of the C═O stretching and (c) the region below the latter.

2.1.1. (a) X—H stretching modes (X = C and N)

2.1.1.1. (a.1) N—H stretching (a_1). The intense band at 3482 cm^{-1} of the IR spectrum of maleimide in the vapor phase and 3486 cm^{-1} in argon matrix is due to the N—H stretching, whereas the MP2 and B3LYP calculated values not including the anharmonicity correction are 3710 cm^{-1} and 3655 cm^{-1}, respectively. These values differ by ca. 228 cm^{-1} and 173 cm^{-1} to the experimental one. After correction, these differences fall to ca. 57 cm^{-1} for MP2 and 7 cm^{-1} for B3LYP. With respect to IR intensity, B3LYP and MP2 values, for this mode, confirm a strong intensity of 91.5 km mol^{-1} and 104.5 km mol^{-1}, respectively. This intensity can be adequately interpreted by Eq. (1) [22] shown below:

$$A^{\mathrm{NH,str.}} = K\left(q_{\mathrm{H}}^{0} + \left(\frac{\partial q_{\mathrm{H}}}{\partial R_{\mathrm{N-H}}}\right)\cdot R_{\mathrm{N-H}}^{0}\right)^{2} \quad (1)$$

where $K = 975$ for intensity values in km mol^{-1}, $R^0_{\mathrm{N-H}}$ stands for the equilibrium N—H bond length and q^0_{H} represents the hydrogen equilibrium charge, which is obtained from the Mulliken net charge corrected by the inclusion of overlap term from the CCFO model [20,21]. This means that the hydrogen charge is given by the p^{xx}_{H} element of the atomic polar tensor [23] of the hydrogen atom, where the '*x*' axes is perpendicular to the molecular plane. The derivative $\partial q_{\mathrm{H}}/\partial R_{\mathrm{N-H}}$ is the rate of variation of this charge with the stretching of the N–H bond. Previous works [22,24] have shown that this latter is small and negative for acid hydrogen atoms, i.e., ≡C—H, ═N—H and —O—H. Their values are situated between −0.01 e $Å^{-1}$ and −0.03 e $Å^{-1}$. For the N—H oscillator, it is −0.02 e $Å^{-1}$ using B3LYP and MP2 calculations with large basis sets, including polarization and diffuse functions [14]. Here B3LYP and MP2 values for the p^{xx}_{H} element of the hydrogen atom in N—H are 0.328 e and 0.342 e, whereas their corresponding values for the $R^0_{\mathrm{N-H}}$ equilibrium distance are 1.011 Å and 1.010 Å, respectively. Using these values in Eq. (1), B3LYP and MP2 predicted intensities for the N—H stretching are 92.4 km mol^{-1} and 101.0 km mol^{-1}, respectively, which are in excellent agreement with the calculated ones.

Table 1

MP2/6-31++G(d,p) and B3LYP/6-31++G(d,p) anharmonic and harmonic optimized geometries of maleimide. B3LYP values are shown in parenthesis. Experimental values are given for comparison from Ref. [4]. Bond angles and distances are given in Å and degrees, respectively.

Parameter	Harmonic	Anharmonic	Experimental
H—C	1.079 (1.082)	1.081 (1.085)	1.091[a]
H—N	1.010 (1.011)	0.999 (1.004)	1.020[a]
C═C	1.346 (1.339)	1.349 (1.343)	1.344 ± 0.004
C—C	1.498 (1.504)	1.504 (1.509)	1.508 ± 0.003
C—N	1.396 (1.397)	1.403 (1.403)	1.409 ± 0.003
C═O	1.224 (1.214)	1.224 (1.215)	1.206 ± 0.002
C—N—C	111.7 (111.6)	111.4 (111.6)	112.0 ± 0.2
N—C—C	105.4 (105.4)	105.5 (105.4)	106.8 ± 0.2
N—C═O	126.3 (126.3)	126.2 (126.3)	123.9 ± 0.3
H—C—C(O)	122.1 (121.8)	122.1 (121.8)	–

[a] Assumed parameters as in Ref. [4].

2.1.1.2. (a.2) C—H stretchings. The symmetric (a_1) and asymmetric (b_2) C—H stretching modes fall at 3104 cm^{-1} and 3170 cm^{-1}, respectively, of the IR spectrum of maleimide in CCl_4/CS_2 solution [10]. The symmetric mode in the vapor phase falls at 3090 cm^{-1}, which is in very good agreement with the one in solution. It is interesting to point out that our B3LYP and MP2 calculations without anharmonicity correction indicate that the C—H symmetric stretching frequency value is greater than the asymmetric one, in contrast to what was found in Ref. [10]. For instance, B3LYP values for the symmetric and asymmetric C—H stretching frequencies are 3270 cm^{-1} and 3250 cm^{-1}, respectively. After anharmonicity correction, B3LYP values indicate to order verified in Ref. [10]. Its C—H symmetric stretching frequency including anharmonicity is 3069 cm^{-1} whereas the corresponding C—H asymmetric frequency is 3111 cm^{-1} in agreement with the experimental one. As expected, we can notice from Table 2 that the anharmonicity effect is much pronounced on these C—H stretching modes.

These symmetric and asymmetric C—H stretching intensities can also be adequately interpreted by using Eq. (1). We have seen that acid hydrogen atoms possess q^0_{H} large and positive whereas $\partial q_{\mathrm{H}}/\partial R_{\mathrm{N-H}}$ is small and negative, and consequently, their X—H stretching intensities are mainly determined by hydrogen atomic charge. In C—H ethylenic hydrogen atoms, the situation is altered due to the increase of the charge-flux term. This latter becomes large and negative, and consequently, the charge and charge-flux terms are practically cancelled, i.e., $q^0_{\mathrm{H}} \cong -(\partial q_H/\partial R_{\mathrm{C-H}})$. As a result, their intensities are generally weak or very weak, as can be seen in Table 2. Another example, the sum of the symmetric and asymmetric C—H stretching intensities in *cis*-$C_2H_2F_2$ is only 3.5 ± 3.5 km mol^{-1} [25].

The p^{xx}_{H} element representing the hydrogen atomic charge of the hydrogen atom in the ethylenic moiety in maleimide is 0.155 e for B3LYP and 0.163 e for MP2. The $\partial q_{\mathrm{H}}/\partial R_{\mathrm{C-H}}$ charge-flux term can be obtained from the expression derived in Ref. [22], as shown to follow:

$$\frac{\partial q_{\mathrm{H}}}{\partial R_{\mathrm{C-H}}} = -\frac{[p^{zy}_{\mathrm{H}} - (p^{zz}_{\mathrm{H}} - p^{xx}_{\mathrm{H}})\cdot tg(\beta)]}{R^0_{\mathrm{C-H}}\cdot tg(\beta)} \quad (2)$$