Feature article

Delocalized electrons in infrared intensities

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HIGHLIGHTS

- How the IR intensities of strongly IR-active modes are generated is described.
- Coupled nuclear and electronic motions are shown schematically and theoretically.
- Intermolecular charge flux induces IR intensity enhancement upon H and X bonding.

ARTICLE INFO

ABSTRACT

In the sense that the main features of infrared (IR) spectra are governed by strongly IR active modes, one needs to know how those strong IR intensities are generated, in order to fully extract the information on the properties of molecular systems from their vibrational spectra. In fact, for many of those modes, the IR intensities arise mainly from the *charge flux* term, meaning that delocalized electronic motions are strongly coupled. The present article shows how we can understand those electronic motions qualitatively by simple schemes, and quantitatively on the basis of well founded theories, especially by analyzing the *electron density derivatives*. The cases of the peptide group, hydrogen-bonded water, and an aromatic hydrocarbon are shown as typical examples.

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1. Introduction

To fully extract the information on molecular systems from their vibrational spectra, it is preferable to take into account all the main factors that determine the spectral profiles. While the vibrational frequencies (including the frequency shifts induced by environmental effects) and the band widths are associated with the horizontal axis of the spectra, the intensities refer to the vertical axis. In the present study, we focus on the vibrational modes with strong infrared (IR) intensities, and describe how the strong IR intensities are generated by the electronic motions that are coupled to the nuclear motions of those modes.

IR intensity is proportional to the square of the dipole derivative $\partial \boldsymbol{\mu}/\partial Q$, which is the derivative of the dipole moment $\boldsymbol{\mu}$ of the system by the vibrational coordinate Q. There are largely two mechanisms that generate this dipole derivative. This is reasonably recognized by the following expansion formula. By using the partial charge q_j and the location $\boldsymbol{r}_j$ of each atomic site j ($1 \leqslant j \leqslant N$, where N is the number of atomic sites in the system), $\boldsymbol{\mu}$ is expanded as

$$\boldsymbol{\mu} = \sum_{j=1}^{N} q_j \boldsymbol{r}_j \qquad (1)$$

Then, $\partial \boldsymbol{\mu}/\partial Q$ is expressed as

$$\frac{\partial \boldsymbol{\mu}}{\partial Q} = \sum_{j=1}^{N} q_j \left(\frac{\partial \boldsymbol{r}_j}{\partial Q} \right) + \sum_{j=1}^{N} \boldsymbol{r}_j \left(\frac{\partial q_j}{\partial Q} \right) \qquad (2)$$

The first term on the right-hand side represents the contribution of the displacements ($\partial \boldsymbol{r}_j/\partial Q$) of the atoms with partial charges q_j, and is called the equilibrium charge term [1–3]. The second term represents the contribution of the changes in the charge distribution ($\partial q_j/\partial Q$) within the system induced by the vibration. In the latter case, if a certain atomic site has a positive value of $\partial q_j/\partial Q$, there should inevitably be (an)other atomic site(s) with negative $\partial q_j/\partial Q$, so that a flux of delocalized electric charges (called a charge flux [1–3]) is generated. This charge flux gives rise to dipole derivative because of the difference in the atomic locations $\boldsymbol{r}_j$. This is why the second term of Eq. (2) is called the charge flux term. The importance of this charge flux term has been recognized, for example, in explaining the negative sign of the dipole derivative of the CH stretching mode in many hydrocarbons, arising from partial cancellation between the positive equilibrium charge term (because hydrogen is positively charged) and the negative charge flux term [4,5].

The equilibrium charge term gives rise to at most a modest magnitude of IR intensity. For example, in the case where two atomic sites with $q_j = \pm 0.5\ e$ are vibrating, the equilibrium charge term gives rise to $\partial \boldsymbol{\mu}/\partial Q$ of $\sim$2.4 D Å^{-1} amu$^{-1/2}$ if the reduced mass

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of the mode is ∼1 amu (as for the CH or OH stretching mode), or ∼0.92 D Å^{-1} amu$^{-1/2}$ if the reduced mass is ∼6.9 amu (as for the C=O stretching mode), the IR intensity associated with it being ∼240 km mol^{-1} or ∼36 km mol^{-1}, respectively. Strongly IR active modes typically have much stronger IR intensities, even if the atomic partial charges are estimated to be smaller, resulting in the idea that, for those modes, the IR intensities arise mainly from the charge flux term. This means that electronic motions are strongly coupled to those modes, and those motions are delocalized in the system.

In the next sections, we describe how we can understand these situations qualitatively by schematic representations of resonance structures, and quantitatively on the basis of well founded theories.

2. Understanding based on schematic representations

For many molecular systems having strongly IR active vibrational modes, the forms of those modes and the electronic motions induced by them are qualitatively understood by schematic representations of resonance structures. Figs. 1 and 2 show some typical example cases, i.e., a protonated retinal Schiff base [*N*-methyl(all-*trans*-retinylidene)ammonium ion], linear and aromatic push–pull type compounds [7-dimethylamino-2,4,6-heptatrienal and 4-(dimethylamino)benzonitrile], the peptide group (*N*-methylacetamide), and a radical cation of a polycyclic aromatic hydrocarbon (the naphthalene radical cation).

In the case of the protonated retinal Schiff base, the most stable structure is normally represented as shown on the lower-right side of Fig. 2(a), where the positive charge arising from the protonation is located on the N atom, which is the protonation site. Another (less stable) structure is obtained by reversing the bond alternation of the conjugated chain [6,7], as shown on the upper-left side of Fig. 2(a), where the positive charge is located on a carbon atom of the ionone ring. Then, this resonance structure scheme indicates that the nuclear displacements between the two structures (constituting the bond alternation mode [7–10]) gives rise to a long-ranged shift of electric charge from one side of the chain to the other, accompanying a significant change in the molecular dipole moment. As a result, the bond alternation mode has a large dipole derivative, giving rise to a strong IR intensity. Indeed, this molecule is calculated (at the B3LYP/6-31+G(2df,p) level, using Gaussian 03 [11]) as having a strongly IR active mode (∼4330 km mol^{-1}) at 1517 cm^{-1} as shown in Fig. 1(a), and its vibrational pattern is essentially quite similar to the bond alternation mode. In other words, the strong IR intensity of this mode [12] is qualitatively understood by the scheme shown in Fig. 2(a).

In the case of a linear push–pull type compound (7-dimethylamino-2,4,6-heptatrienal) [8] also, the bond alternation mode gives rise to a long-ranged shift of electric charge, and hence, a strong IR intensity. In this case, the most stable structure is normally represented as shown on the upper-left side of Fig. 2(b), where the lone pair of electrons is located on the N atom. As a
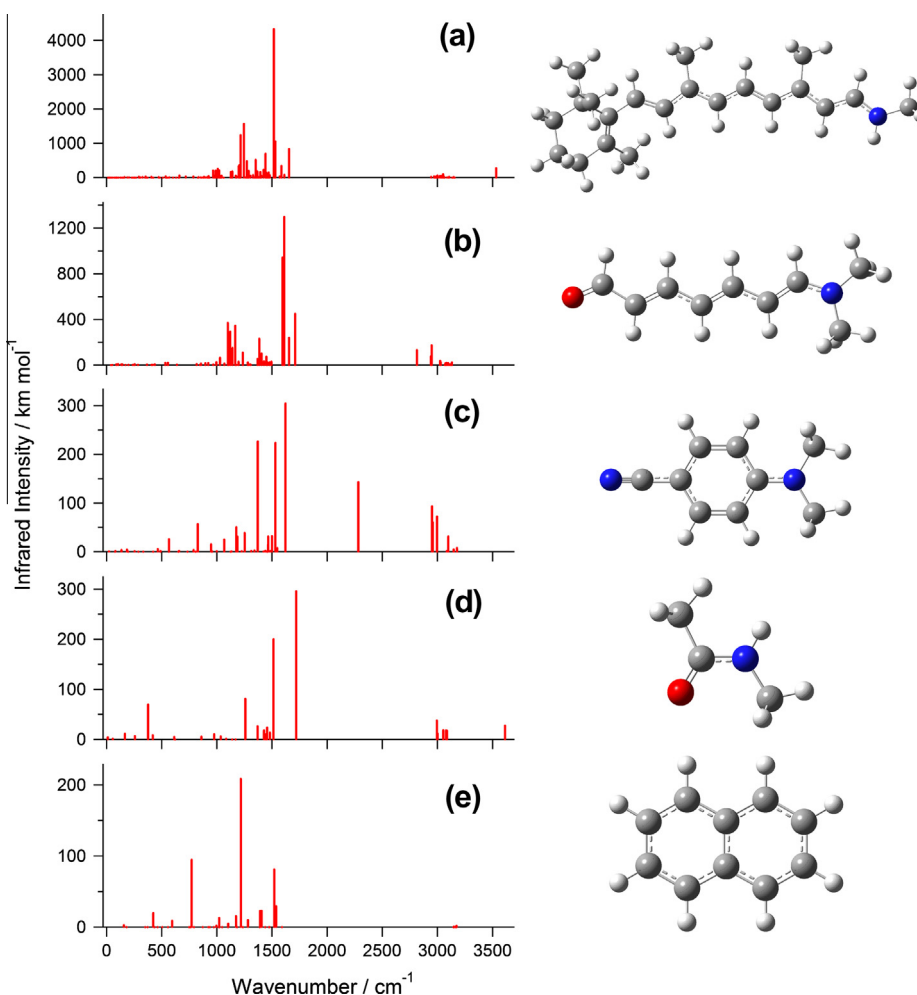

Fig. 1. Infrared spectra of (a) *N*-methyl(all-*trans*-retinylidene)ammonium ion, (b) 7-dimethylamino-2,4,6-heptatrienal, (c) 4-(dimethylamino)benzonitrile, (d) *N*-methylacetamide, and (e) the naphthalene radical cation calculated at the B3LYP/6-31+G(2df,p) level, with the frequencies being scaled by 0.9860. The molecular structure of each compound is shown on the right-hand side.