

Differential ion mobility separation of isomers for threshold collision-induced dissociation measurements



John P. van Nostrand, Vladimir Romanov¹, Justin Kai-Chi Lau, Udo H. Verkerk*, Alan C. Hopkinson, K.W. Michael Siu

Department of Chemistry and Centre for Research in Mass Spectrometry, York University, 4700 Keele Street, Toronto, Ontario, Canada M3J 1P3

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ABSTRACT

A triple-quadrupole mass spectrometer adapted for threshold-collision-induced dissociation (TCID) measurements was modified by replacing the standard mass spectrometer front-end with a Fernandez de la Mora-type differential mobility analyzer (DMA). Using a combination of a drift field and an orthogonal laminar gas flow at atmospheric pressure, an ion of a given mobility (DMA voltage) can be isolated from a continuous stream of electrosprayed ions for TCID measurements. Proof-of-concept DMA-TCID experiments using silver complexes of mixtures of *ortho-para* and *cis-trans* isomers as well as silver complexes of the individual isomers show excellent agreement in the determined bond dissociation energies (BDEs) between both sets of experiments as well as with theoretical BDEs predicted by density functional theory.

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1. Introduction

With the advent of electrospray ionization [1] it has become possible to transfer ions of widely varying size and complexity into the gas phase and examine these ions in the absence of solvent interactions by physical and chemical means. The selection of gas-phase ions targeted for analysis is often solely based on the mass-to-charge ratio, so simultaneous sampling of isobaric isomers cannot be excluded. Such a mixture may consist of a thermal distribution or kinetically trapped structures of higher energies, depending on chemical and instrumental factors. Bond dissociation energies (BDEs) determined for mixtures of isomers are not easily deconvoluted [2,3].

The presence of isomers in mixtures in mass spectrometry is most clearly demonstrated by IRMPD [4–9] and IR-UV double resonance [10–12] spectroscopic experiments; here a comparison of well-separated spectral bands in combination with shifts observed by isotope labeling, and predicted bands from density functional theory (DFT) modeling, allow assignment of different isomers. DFT modeling can assist in identifying potential interference of isomers based on the energies of, and interconversion barriers between,

isomers. However, the complexity of these computations increases rapidly with the number of atoms in the ions. In addition to being sensitive to the dimensions of the conformational landscape, the outcome of density functional modeling also depends on functional and basis set selection [13–15]. A physical separation of the isomers would greatly simplify identification and investigation of chemical properties of individual isomers.

To reduce conformer overlap in IR-UV double resonance experiments, Papadopoulos et al. used an atmospheric gas-phase separation method based on field asymmetric waveform ion mobility spectrometry (FAIMS) before trapping, cooling and spectroscopic interrogation of the ions [16]. A simplification of the congested electronic spectrum was achieved, but some conformational isomerization before recording of the spectrum did occur. Isomerization of ions likely results from the high RF and DC fields [17] required for FAIMS, which facilitated collisional heating and interconversion at atmospheric pressure. A low-energy gas-phase isomer separation followed by mass selection would be preferred for simplifying IR/UV spectroscopic and bond-energy measurements on isomer mixtures or electronic states of transition metals [18–20].

Like the FAIMS, the parallel-plate differential mobility analyzer (DMA) is a spatial filter that selects ions of specific mobility from a continuous stream of ions. Unlike the FAIMS, the DMA is a low energy separation technique that operates at lower field strength than FAIMS. Calculations of T_{eff} [21] indicate that ions pass through the DMA at 30 °C, and experience less than 2.5 °C of heating by the electric field, suggesting use of the DMA for isomer separation. In

* Corresponding author. Tel.: +1 416 650 8426.

E-mail addresses: uwerkerk@yorku.ca (U.H. Verkerk), kwmsiu@yorku.ca (K.W.M. Siu).

¹ Present address: Smiths Detection Toronto, 7030 Century Avenue, Mississauga, Ontario, Canada.

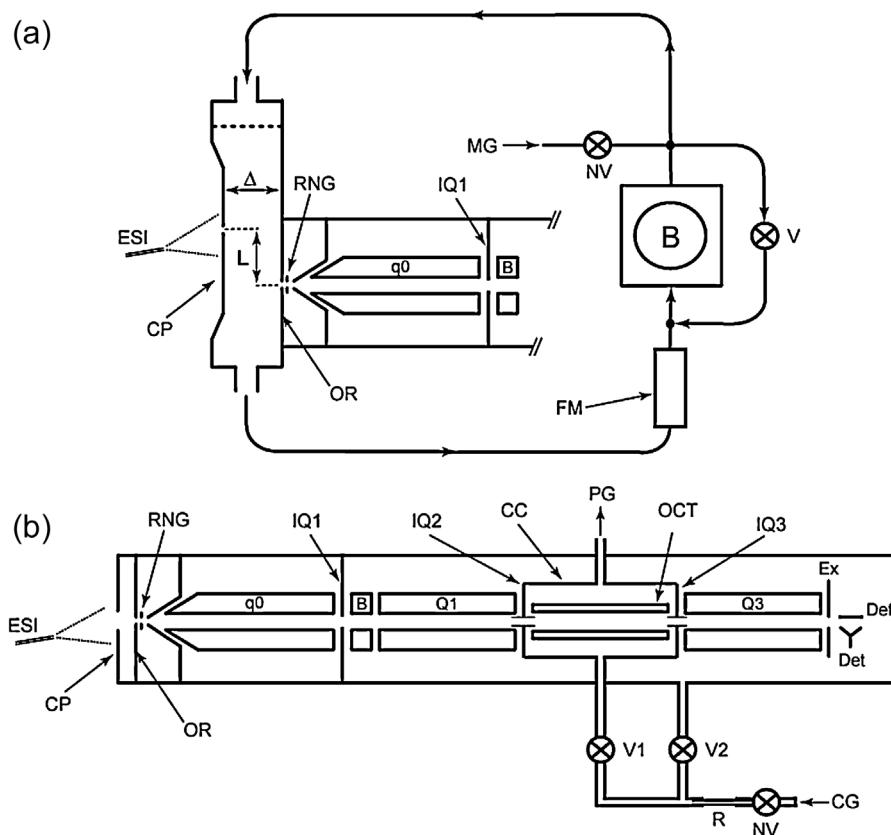


Fig. 1. (a) Front end of the API 365 with differential mobility analyzer (DMA) mounted. Separation is effected by applying a voltage difference over the curtain plate (CP) and the orifice plate (OR). Electrosprayed ions entering the space between CP and OR are mobility separated by drifting through the orthogonal laminar gas flow supplied by blower (B) over a distance determined by the interplate distance (Δ) and the offset (L) between the entrance slit and the orifice. The flow rate can be measured using the mass flow meter (FM) and adjusted using a bypass valve (V). Solvent vapor is prevented from entering the DMA by maintaining a positive gas pressure using a make up gas flow (MG) that is adjusted using a needle valve (NV); a flow rate of 200 L/min was used in the DMA experiments. (b) API 365 triple-quadrupole mass spectrometer used for threshold collision-induced dissociation: curtain plate (CP), orifice plate (OR), ring electrode (RNG), collision gas (CG), valve (V1), bypass valve (V2), needle valve (NV), restrictor (R), pressure gauge (PG), Brubaker lens (B), inter quad lenses (IQ1,2,3), collision cell (CC), octapole ion guide (OCT), deflector (Def), detector (Det), extraction lens (Ex).

a parallel-plate DMA, separation takes place when gas-phase ions enter through a slit in the curtain-plate of the DMA and move under the influence of an electric drift field through an orthogonal laminar flow of nitrogen gas between the parallel plates (see Fig. 1a). As the electric field moves the ions across the gas flow over a distance Δ toward the sampling orifice of the mass spectrometer, the gas flow simultaneously moves the ions downstream over a distance L . Under these forces a fan-like trajectory is produced for ions predominantly following the gas flow (low mobility ions) and for ions predominantly following the electric field (high mobility ions). The slope of the individual ion trajectories is proportional to the ion-mobility (see Eq. (1), with U being the gas velocity, V_{DMA} the potential difference between the plates, and Z the ion mobility in $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$), with the point of impact on the counter electrode determined by the electric field at constant gas velocity.

$$Z = \frac{U\Delta^2}{LV_{\text{DMA}}} \quad (1)$$

By adjusting the electric field, ions of a specific mobility can be projected on the mass spectrometer orifice located at $L=11$ mm and $\Delta=6$ mm from the slit in the curtain plate. Large ions of lower mobility Z require a higher voltage difference V_{DMA} between the plates to reach the inlet to the mass spectrometer compared to small ions of higher mobility at the same charge. Unlike drift-time or classical ion-mobility mass spectrometry, where ion packets are separated in time, this spatial mobility filter selects ions based on the magnitude of the applied field $E=V_{\text{DMA}}/\Delta$, which renders

a mobility-separated ion stream for downstream thermodynamic measurements.

Recently, we implemented and validated threshold collision-induced dissociation (TCID) [22] measurements on a commercially available triple-quadrupole mass spectrometer [23]. TCID is an established method for obtaining accurate bond-dissociation energies (BDEs) [24,25] that has been pioneered by Armentrout and co-workers [26–28]. The BDE of a non-covalent metal complex is the enthalpy change ΔH°_T of the dissociation reaction (see Scheme 1) at temperature T , typically 0 K. Herein we describe the adaptation of a triple-quadrupole-based mass spectrometer for use in isomer-selection TCID experiments using a combination of a parallel-plate DMA as the isomer selector and an octapole ion guide as the collision cell for TCID. Bond-energy measurements of silver complexes with (1) mixtures of *ortho/para* dicyanobenzene: 1,2-dicyanobenzene (abbreviated *o*-DCB) and 1,4-dicyanobenzene (*p*-DCB), and (2) mixtures of the *cis/trans* isomers: dimethyl (*Z*)-but-2-enedioate (*c*-DMBD) and dimethyl (*E*)-but-2-enedioate (*t*-DMBD) (see Scheme 1) were used for proof-of-concept experiments.

2. Methods

Sample solutions were prepared to contain 15–100 μM ligand and 35 μM silver nitrate in 20/80 water/methanol. All chemicals were purchased from Sigma–Aldrich (St. Louis, MO) and were used as received. Concentrations of the ligand were adjusted to result

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